STUDIES ON
THE REACTIONS OF (NSCl)₃, NSOH, NOX
(X = Cl, Br, Br₃, NO₂) WITH SOME
TRANSITION METAL COMPLEXES (Ru, Rh, Ir, Pd & Pt)
and
CYCLIC VOLTAMMETRIC STUDIES ON (NSCl)₃

By

KAILASH CHAND JAIN
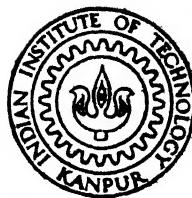
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
DECEMBER, 1981

STUDIES ON
THE REACTIONS OF $(NSCl)_3$, NSOH, NOX
$(\bar{X} = Cl, Br, Br_3, NO_2)$ WITH SOME
TRANSITION METAL COMPLEXES (Ru, Rh, Ir, Pd & Pt)
and
CYCLIC VOLTAMMETRIC STUDIES ON $(NSCl)_3$

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
KAILASH CHAND JAIN

to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
DECEMBER, 1981

JAN-1951-D-JAN-III

To The Loving Memory

of

My Father

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Prof. U.C. Agarwala.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Kailash Chand Jain

KAILASH CHAND JAIN

CERTIFICATE

Certified that the work contained in this thesis, entitled: STUDIES ON THE REACTIONS OF $(NSCl)_3$, NSOH, NOX (X = Cl, Br, Br_3, NO_2) WITH SOME TRANSITION METAL COMPLEXES (Ru, Rh, Ir, Pd and Pt) AND CYCLIC VOLTAMMETRIC STUDIES ON $(NSCl)_3$ has been carried out by Mr. Kailash Chand Jain, under my supervision and the same has not been submitted elsewhere for a degree.

(U.C. AGARWALA)
Professor of Chemistry,
Thesis Supervisor

Kanpur
December 1981.

DEPARTMENT OF CHEMISTRY,
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR, INDIA

CERTIFICATE OF COURSE WORK

This is to certify that Mr. Kailash Chand Jain has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 500   Advanced Organic Chemistry I
Chm 511   Physical Organic Chemistry
Chm 524   Modern Physical Methods in Chemistry
Chm 541   Advanced Inorganic Chemistry
Chm 800   General Seminar
Chm 801   Graduate Seminar
Chm 900   Post-Graduate Research

Mr. Kailash Chand Jain was admitted to the candidacy of the Ph.D. degree programme in March , 1978 after he successfully completed the written and oral qualifying examinations.

(U.C. Agarwala)   (N. Sathyamurthy)
Head,   Convener,
Department of Chemistry   Departmental Post-
I.I.T., Kanpur   Graduate Committee
                                        Dept. of Chemistry,
                                            I.I.T., Kanpur

ACKNOWLEDGEMENTS

KAILASH CHAND JAIN

Kanpur
December 1981.

PREFACE

It is now a truism that, in the last two decades, the transition metal ions have been able to stabilize a few of the unstable small molecules like NO, CS, SO by coordinating with them in presence of other ligands. It has stimulated the interest of contemporary inorganic chemists in their potential application in organic and inorganic syntheses, using them as catalysts in various reactions and in understanding the nature of biological processes. The present work encompasses the chemistry of stabilization of NS as derived from $(NSCl)_3$, NSOH and NO, using N_2O_3, NOCl, NOBr, $NOBr_3$ as nitrosylating agents by a few platinum metal ion complexes (Ru, Rh, Ir, Pt, Pd). Besides these, the electrochemical behaviour of trithiazyltrichloride has also been investigated.

The scope, the object of the work and the brief literature survey regarding thionitrosyl complexes of transition metals, nitrosyl complexes of ruthenium, nitro and nitrato complexes of ruthenium, palladium and platinum, thiazate complexes along with the cyclic voltammetric studies on sulfur-nitrogen compounds have been discussed in Chapter I.

The procedures for synthesizing new thionitrosyl complexes of ruthenium, rhodium and iridium and the thiazate complexes of rhodium have been developed which form the subject matter of Chapter II and Chapter III.

Chapter IV deals with the reactions of a few ruthenium complexes with nitrosylhalides and dinitrogentrioxide in presence of tertiary-phosphine, arsine and stibine which resulted in the formation of few new complexes. Their physical and the chemical properties have been studied using various physicochemical techniques. Their possible structures have also been proposed.

Fifth chapter describes the interesting oxidative addition reactions of dinitrogentrioxide with palladium(0) and platinum(0) triphenylphosphine complexes. The interaction of nitrosylhalides and dinitrogentrioxide with palladium(II) and platinum(IV) in presence of tertiary-phosphine and arsine has also been discussed therein.

The fabrication of a simple Cyclic Voltammetric instrument in the laboratory, the studies of electrochemical behaviour of trithiazyltrichloride in different aprotic solvents and the effects of added transition metal complexes thereon have been dealt in Chapter VI.

Chapter VII briefly overviews the work described in the thesis along with a few proposals for future work.

CONTENTS

Contents (contd.)

...

CHAPTER I

INTRODUCTION

Scope and Objective of Work

The chemistry of transition metal nitrosyl complexes is
one that has blossomed during the past three decades. Most
emphasis is laid on developing new synthetic procedures[1-6] and
in understanding the reactivity and the nature of bonding[6-14]
of coordinated nitrosyl group with metal ions. The thionitrosyl
analogues have, however, eluded syntheses until recently. Their
apparent reluctance for syntheses was a result of the lack of
a suitable thionitrosylating agent. Literature shows the
syntheses of only a few thionitrosyl complexes. The first
exploratory work on their syntheses was carried out by Chatt,
et al.[15-17] who synthesized thionitrosyl complexes of ruthenium,
osmium, rhenium, and molybdenum by reacting respective metal
nitrides with either elemental sulfur, propylene sulfide or
disulfur dichloride. Another easier alternative approach for
their syntheses which has been tried later on is by the reaction
of[NSCl]with few transition metal complexes.[18-23] Although

ruthenium forms relatively more nitrosyl complexes than any other metal, only two thionitrosyls of ruthenium have so far been synthesized. Reactions of coordinated thionitrosyl group have not so far been tried.

In addition, another vast and rapidly expanding aspect of transition metal nitrosyl chemistry is that they have been shown to be effective catalysts[25] in a number of reactions. Thus, ruthenium nitrosyls have been used in introducing N-C bond,[30,31] and conversion of poisonous carbon monoxide into dioxide.[24-28] Palladium and platinum nitro complexes in the presence of triphenylphosphine, catalyzed the reactions of Schiff's bases with 1,3-butadiene. $[M(NO_2)_2L_2]$ (M = Pd, Pt; L = PPh_3, PEt_2Ph, PEt_3) were found suitable in the removal of CO from the exhaust gases.[27,34-36]

These aspects of nitrosyl- and nitro-chemistry noted above with meagre information available for the thionitrosyl-complexes have induced us to look into the chemistry of thio-nitrosyl and nitrosyl complexes. The thionitrosyl complexes of ruthenium, rhodium, iridium and nitro-nitrato complexes of palladium and platinum with a possibility of using them further as starting materials[32,33] for obtaining new compounds have been synthesized and characterized.

Second chapter describes the reactions of trithiazyl-trichloride(used as a thionitrosylating agent) with $RuCl_2(PPh_3)_3$, $RuBr_3(AsPh_3)_3$, $RuHCl(CO)(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$. The

structures of the complexes, solvated dichlorodithionitrosyl-
bis(triphenylphosphine), $[RuCl_2(NS)_2(PPh_3)_2].S$ (S = CH_2Cl_2,
$CHCl_3$ or $CHBr_3$) and dichloromononitrosyl-monothionitrosyl-
bis(triphenylphosphine) $[Ru(NO)(NS)Cl_2(PPh_3)_2]$ thus, formed
have been postulated on the basis of i.r., magnetic and other
physicochemical data. The products of the reactions of
$[RuCl_2(NS)_2(PPh_3)_2].S$ with Cl_2, Br_2, I_2, HCl, NOX (X = Cl,
Br, Br_3 or NO_2) and water have been characterised.

The first part of the third chapter describes new routes
for the synthesis of $[Rh(NS)Cl_2(PPh_3)]_2$ along with the reaction
of trithiazyltrichloride with $[IrHCl_2(PPh_3)_3]$ to form $[Ir(NS)Cl_2$-
$(PPh_3)_2]$. The syntheses of thiazate (NSO^-) complexes of rhodium
with the interaction of Rh(I) complexes with NSOH have been
dealt in the second part. The tentative structures of the
resulting compounds $[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$, $[Rh(H_2O)(NSO)_2Cl$-
$(PPh_3)_2]$ and $[Rh(H_2O)CO(NSO)_2Cl(PPh_3)]$ have been assigned on
the basis of analytical, spectral and other physicochemical
studies.

The products of the reactions of $RuCl_3.xH_2O$ with NOX
(X = Cl, Br, Br_3 or NO_2) in presence of triphenylphosphine,
triphenylarsine and triphenylstibine are described in Chapter IV.
Herein the reactions of NOX with some ruthenium complexes have
also been presented whereby compounds of the type $[Ru(NO)ClX_2L_2]$
(X = Cl or Br; L = PPh_3, $AsPh_3$ or $SbPh_3$) and $[Ru(CO)_2X_2(PPh_3)_2]$
(X = Cl or Br) were obtained and characterised.

Chapter five describes the interesting oxidative addition reactions of dinitrogen trioxide with tetrakis(triphenylphosphine)palladium(0) and tetrakis(triphenylphosphine)platinum(0) in presence and absence of oxygen. Reactions of NOX (X = Cl, Br, Br_3) with $Pd(PPh_3)_4$, $PdCl_2$ and H_2PtCl_6 in presence of PPh_3 and $AsPh_3$ have also been described. These reactions resulted in the formation of complexes $[M(NO_2)_2(PPh_3)_2]$, $[M(NO_2)(NO_3)(PPh_3)_2]$, $[MCl_2(PPh_3)_2]$, $[MCl_2(AsPh_3)_2]$ (M = Pd or Pt), $[PdBr_2(AsPh_3)_2]$, $[PdBr_2(PPh_3)_2]$ and $[Pd_2Br_4(PPh_3)_2]$.

Electrochemical behaviour of NO, N_2O_4, NO_2, N_2O_3, etc. have been known for the last twenty years[37-42] but no report pertaining to the studies on their thioanalogues except S_4N_4 is available. Due to the non-availability of a commercial indigenous cyclic voltammetric instrument, a simple cyclic voltammetric set-up has been fabricated by using indigenous materials which forms the first part of Chapter VI. The second part deals with the cyclic voltammetric behaviour of trithiazyltrichloride in acetonitrile and dimethylformamide. Quasireversible behaviour of the redox process, $[NSCl] \rightleftharpoons [NSCl]^{\cdot -}$ was observed and the effects of added transition metal complexes have been investigated.

A brief overview of the work and some proposals to extend it further have been given in Chapter seven.

Although an extensive review on the ruthenium nitrosyl complexes has appeared in 1978, the vast data of the fast

expanding field of nitrosyls needs summarizing till this date. In the following paragraphs, a brief review on the topic is presented with special emphasis on the work related to the understanding of the nature of the bond between metal and the nitrosyl group. Besides,the chemistry of nitro, nitrato, thiazato and thionitrosyl groups have also been briefly reviewed.

The Chemistry of Thionitrosyl Group (NS)

The syntheses, the properties of thionitrosyl radical, its ionic $[NS^+MF_6^-$ $(M = As, Sb)$; $NS^+BF_4^-$, $NS^+Sb_2F_{11}^-]$,[43] covalent $(NSF, NSF_3$ and $NSCl)$ compounds and transition metal thionitrosyl complexes, covering the literature until 1980 have been reviewed by Agarwala, et al.[44]

Thionitrosyl radical with one unpaired electron, unlike its homologue NO, polymerizes so readily that it is not possible to isolate it as monomer solid or liquid and even in the gaseous phase it has only a transient existence.[45] It, similar to NO, can exist as $[NS^+]$[46] or $[NS^-]$[47] by respectively loosing or gaining an electron and many of its properties should therefore be approximately analogous to those of NO. It has low ionization potential[48] (9.85 eV), high dipolemoment[49] (1.86 D). It is paramagnetic having a doublet $2\pi_{1/2}$ ground state and with the lowest excited state, $2\pi_{3/4}$ lying ≈ 223 cm^{-1} above the ground state level. A calculated electronic configuration

of NS is $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi^4\ 2\pi^1$, where the valence electrons of only nitrogen and sulfur are considered. A large number of papers related to its microwave spectra have appeared in the literature[50-66] and the excited valence states $B^2\pi$, $A^2\Delta$, $G^2\Sigma^-$, $H^2\pi$ and $I^2\Sigma^+$ have been identified besides its ground state. Its i.r. spectrum showed a very weak band at 1225 cm^{-1} [67] (vibrational frequency of the gaseous NS molecule[68,69] is given as 1204.1 cm^{-1}). Its e.s.r. spectrum has also been studied.

Glemser, et al.[70,71] in 1971 obtained, for the first time, an ionic compound, $NS^+AsF_6^-$ by the reaction of NSF with AsF_5. Other ionic, salt like compounds, $NS^+SbF_6^-$ and $NS^+BF_4^-$ have also been synthesized by reacting NSF with SbF_5 or BF_3 in liquid SO_2 in 90% yield[72-74] or by reacting trimer or tetramer of NSF with an excess of AsF_5, SbF_5 or BF_3.[75] Both i.r. and Raman spectra showed a band around 1435 cm^{-1} assigned to $\nu_{NS}+$. Reactions of $NS^+AsF_6^-$ with $NO^+(CF_3SO_3)^-$, N_4S_4 and S_2Cl_2 yielded $NS^+(CF_3SO_3)^-$, $S_5N_5^+AsF_6^-$ and $N(SCl_2)^+AsF_6^-$.

Principal covalent compounds of NS are NSF, NSF_3 and NSCl. A comparison of the positions of ν_{NS} observed in the i.r. spectra of NSF[76] (1372 cm^{-1}), NSF_3 (1515 cm^{-1}) and NSCl (1320 cm^{-1}) suggested that the bond order of NS in NSF is lower than that in NSF_3 and higher to that in NSCl (Fig. I.1(b)). Various attempts have been tried in order to establish a relationship between N-S bond distances (r_{NS}) and the bond
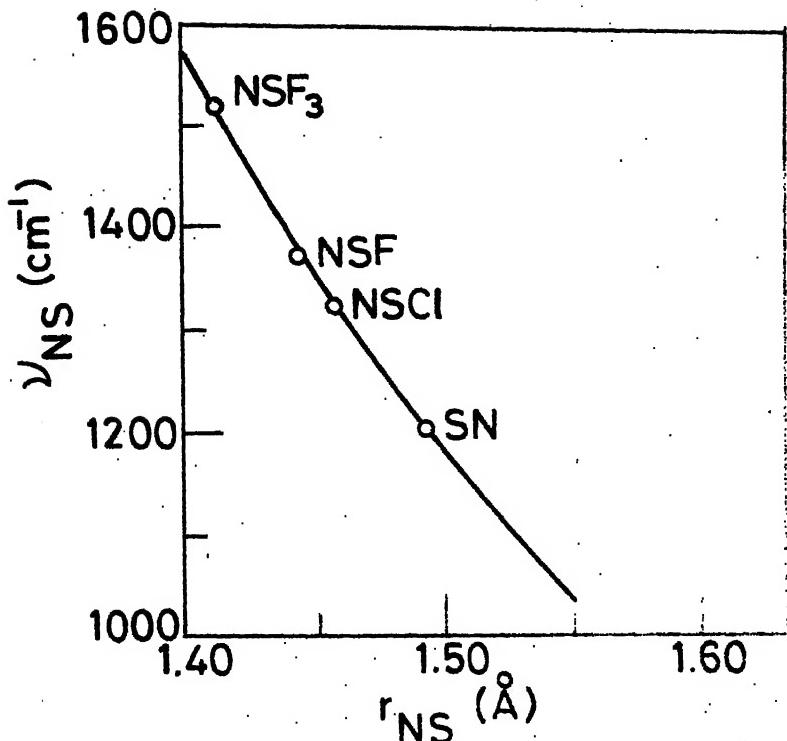
Fig.I.1b   Correlation of S-N stretching
frequencies and bond lengths.
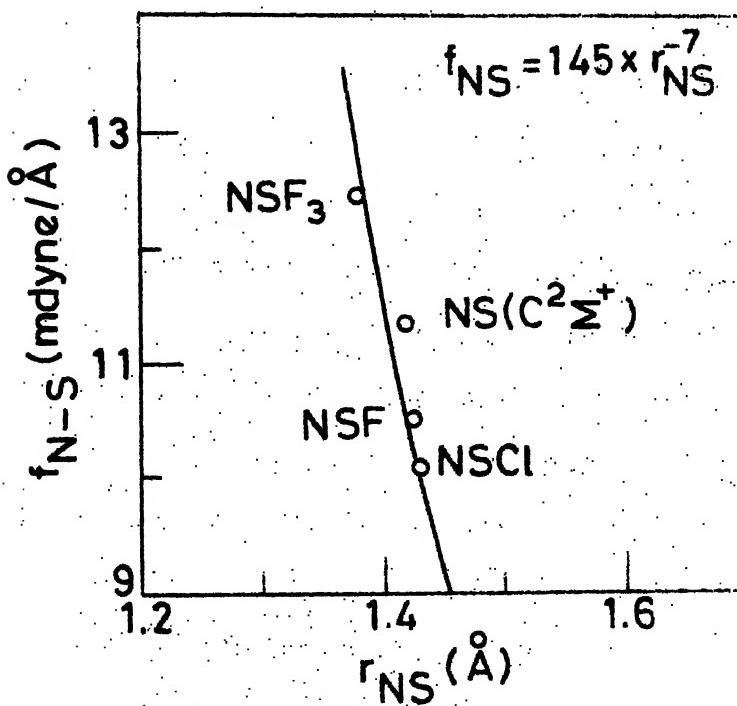
Fig.I.1a   Correlation of force constants
and bond lengths.

orders (η_{NS}) in various covalent compounds (Fig. I.1(a)) to characterize NS bond in NSF, NSF_3 and NSCl, and that resulted in a linear relationship[77-80] between f_{NS} and r_{NS}.

Thionitrosyl chloride [NSCl] is a greenish yellow gas, readily polymerizes to form a stable trimer,[81-83] (3 NSCl $\rightleftharpoons$ $N_3S_3Cl_3$) is highly sensitive to moisture and hydrolyses readily by water to form HNSO, NH_4^+ and SO_3^{2-}.[84]

$$NSCl + H_2O \longrightarrow HNSO + HCl$$

$$HNSO + 2 H_2O \longrightarrow NH_4^+ + SO_3^{2-}$$
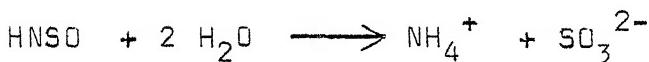
Thionitrosyl Complexes

Although there has been considerable interest in developing the chemistry of thionitrosyl complexes of transition metals during the last five years, it is still in an embryonic state. This is partly due to the lack of suitable reagents that could have been utilized to introduce thionitrosyl group in a complex. However, the present states pertaining to the bonding in thionitrosyl complexes is that these are, analogous to the bonding in nitrosyls, three bonding modes of thionitrosyl group with the metal ions. These are: (a) terminal linear M-N-S, (b) terminal bent M-N-S, and (c) bridging NS. In (a), thionitrosyl is coordinated as NS^+, while in (b), as NS^-.

It is convenient to classify MNS complexes by $\{ MNS \}^n$, where n is the number of d type electrons present in the complex if thionitrosyl is regarded as being coordinated with

metal ion as NS^+. We have preferred to use this classification scheme in the thesis. In the following paragraphs, the existing thionitrosyl complexes are briefly examined with reference to their existence in various coordination numbers.

(i) Seven coordination

The compounds, $[Mo(NS)(S_2CNR_2)_3]$ (R = Me_2, Et_2, $(CH_2)_4]$[15,17] were synthesized by refluxing dioxo-complexes, $[MoO_2(S_2CNR_2)_2]$ with trimethylsilylazide in presence of elemental sulfur in acetonitrile. It seemed likely that the reaction proceeded via intermediate formation of nitrido complex, $[MoN(S_2CNMe_2)_3]$ which subsequently reacted with elemental sulfur to give the corresponding thionitrosyl complex. Its ^{1}H-NMR spectrum at

$$[MoN(S_2CNMe_2)_3] + S_8 \xrightarrow[\text{reflux}]{CH_3CN} [Mo(NS)(S_2CNMe_2)_3]$$
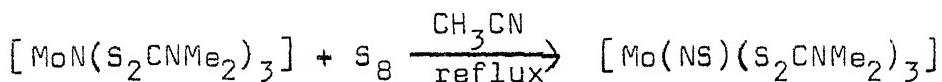
room temperature in nitrobenzene showed a triplet (1:2:3) due to dithiocarbamate methyl groups. Its structure is pentagonal bipyramid with a linear apical NS group, (Mo-$\widehat{N}$-S, 172.0(7)°; Mo-N, 1.73 Å; N-S, 1.59 Å).[86] Comparison of thionitrosyl complex with its nitrosyl analogue[86] indicated the same M-N distance and M-$\widehat{N}$-X (X = S, O) angle in both the complexes. Its reaction with triphenylmethyltetrafluoroborate yielded $[Mo(NSCPh_3)(S_2CNR_2)_3] \cdot BF_4$. These complexes have been desulfurized by refluxing them with PBu_3^n in toluene or acetonitrile to form the parent nitrido complexes.

(ii) <u>Six coordination</u>

The six coordinate complexes so far prepared are mono-thionitrosyls.

<u>Ruthenium complexes</u>: The syntheses of two ruthenium thionitrosyl complexes,[Ru(NS)Cl$_3$L$_2$] (L =PPh$_3$ or AsPh$_3$) so far known, have been carried out by reacting RuCl$_3$.xH$_2$O with (NSCl)$_3$ in THF or in CCl$_4$-CHCl$_3$ mixture in presence of triphenylphosphine or triphenylarsine[19]:

$$[RuCl_3.xH_2O] + \tfrac{1}{3}(NSCl)_3 + L \xrightarrow{\text{THF}} [Ru(NS)Cl_3L_2]$$
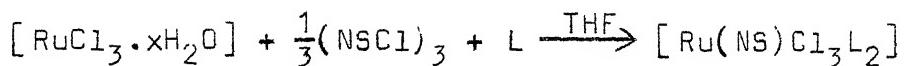
Their i.r. spectra showed a strong sharp absorption band in 1290-1295 cm^{-1} region assigned to ν_{NS}+. X-ray structure determination[87] of arsine analogue has shown Ru-N-S angle to be 179°, suggesting NS ligand as three electron donor. Similarly, other six coordinated{ RuNS}^{6} complexes have also been regarded as the ones of Ru(II) with NS$^+$.

<u>Rhodium complexes</u>

Six coordinated diamagnetic rhodium complexes, [Rh(CO)-(NS)Cl$_2$L$_2$] (L = PPh$_3$ or AsPh$_3$) have recently been synthesized[20,21,23] by the reactions of trithiazyl trichloride with trans-[Rh(CO)-ClL$_2$] in THF.

$$\text{Trans-}[Rh(CO)ClL_2] + \tfrac{1}{3}(NSCl)_3 \xrightarrow{\text{THF}} [Rh(CO)(NS)Cl_2L_2]$$
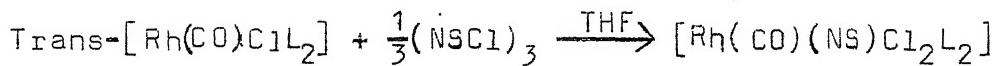
Reaction of [RhH(CO)(PPh$_3$)$_3$] with (NSCl)$_3$ in carbon tetrachloride chloroform mixture yielded a deep green chlorobridged complex,

$[Rh(CO)(NS)Cl_2(PPh_3)]_2$ which with an excess of triphenylphos-
phine or triphenylarsine in CH_2Cl_2 gave as a result of cleavage
of chlorobridge yellowish orange complexes, $[Rh(CO)(NS)Cl_2L_2]$-
$\frac{1}{2}CH_2Cl_2$. Their infrared spectra showed absorption bands in
the range 2100-2110 cm^{-1} (ν_{CO}), 1118-1120 cm^{-1} (ν_{NS}), 330 cm^{-1}
(terminal ν_{Rh-Cl}) and a band at 260 cm^{-1} of the green complex
was assigned to the bridged ν_{Rh-Cl}. The six coordinated
{RhNS}[8] complexes have been regarded as complexes between
Rh(III) and NS$^-$. The probable structures assigned to $[Rh(CO)$-
$(NS)Cl_2(PPh_3)]_2$ (I) and $[Rh(CO)(NS)Cl_2(PPh_3)_2]$ (II) are:
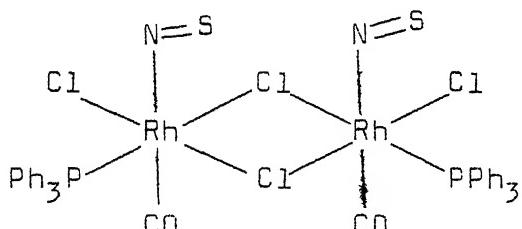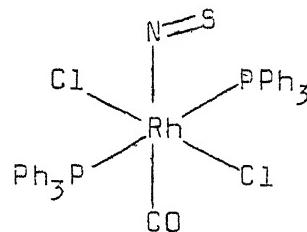
(I)   (II)

Reactions of $[Rh(CO)(NS)Cl_2L_2]$ with NOCl in CH_2Cl_2 afforded
the corresponding nitrosyl complexes, $[Rh(CO)(NO)Cl_2L_2]$.

Rhenium complexes: Reactions of S_2Cl_2 with $[ReNCl_2(PRPh_2)_2]$
(R = Ph or pr^n)[17] and $[ReX_2N(PR_3)_3]$ (PR$_3$ = PMe$_2$Ph, PEt$_2$Ph or
PMePh$_2$; X = Cl or Br) resulted in the formation of the corres-
ponding thionitrosyl complexes, $[Re(NS)Cl_3(PRPh_2)_2]$ and
$[Re(NS)ClX_2(PR_3)_2]$ respectively. S_2Cl_2 also reacted with
$[ReClN(dppe)_2]Cl$ (dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) to yield

$[Re(NS)Cl(dppe)_2]Cl$ and which in turn reacted with $FeCl_3$ or NH_4PF_6 with the formation of $[Re(NS)Cl(dppe)_2]X$ (X = $FeCl_4^-$, PF_6^-). The i.r. spectra of $[Re(NS)Cl(NCS)(PMe_2Ph)_3]$ and $[Re(NS)Cl(PMe_2Ph)_2(S_2CNMe_2)]$, synthesized by treating $[Re(NS)Cl_2(PMe_2Ph)_3]$ with KCNS and $Na(S_2CNMe_2)$ respectively, showed a single strong band in the region, 1167-1185 cm^{-1} suggesting the presence of coordinated NS^+ group in these complexes. X-ray crystal structure analysis of the analogous nitrosyl complex, $[Re(NO)Cl_2(PMe_2Ph)_3]$[88] showed Re-$\widehat{N}$-O angle, 178.8 (1.4)^0 indicating the possibility of linear Re-N-S group also in the thionitrosyl analogue.

Osmium complexes: $[OsClX_2NL_2]$, (L = $AsPh_3$, $PMe_2(C_6H_5)$ or 2,2'-bipyridyl) reacted with half an equivalent of S_2Cl_2 with the formation of thionitrosyl complexes, $[Os(NS)ClX_2L_2]$, (X = Cl, Br).[17] $[Os(NS)Cl_3(Py)_2]$ was prepared by adding pyridine (Py) to a CH_2Cl_2 solution of the product of the reaction between $[NBu_4][OsCl_4N]$ and S_2Cl_2. $[Os(NS)Cl_3L_2]$ (L = PPh_3 or $AsPh_3$[19] have been synthesized by reacting $(NSCl)_3$ with $OsCl_3 \cdot xH_2O$ in THF in presence of triphenylphosphine and triphenylarsine. A band of medium intensity was observed in their i.r. spectra in the range, 1270-1295 cm^{-1} indicating the presence of coordinated NS^+ group.

Iridium complexes: Until recently, only one reddish brown thionitrosyl complex of iridium, $[Ir(CO)(NS)Cl_2(PPh_3)_2]$ has been synthesized by reacting $(NSCl)_3$ in THF with $[Ir(CO)Cl(PPh_3)_2]$,

whose i.r. spectrum showed absorption bands at 2050 cm^{-1} (ν_{CO})
and 1110 cm^{-1} (ν_{NS}-). Shift in the position of ν_{CO} towards
higher frequency (2050 cm^{-1}) in $[Ir(CO)(NS)Cl_2(PPh_3)_2]$ is
reasonable for iridium(III) system and.is possibly influenced
by the strong primarily π-bonding trans effect of the trans NS$^-$
group.

Reaction of $(NSCl)_3$ with $[Ir(CO)Cl(PPh_3)_2]$ in oxygen
atmosphere yielded a bright green compound, $[Ir(CO)(NSO)Cl_2$-
$(PPh_3)_2]$which was the first thiazate complex to be synthesized.
However, the same compound was also obtained by reacting
$[Ir(CO)Cl(O_2)(PPh_3)_2]$ with $(NSCl)_3$ in THF.[89]

Five Coordination

The reactions of $(NSCl)_3$ in THF with $[RhX(PPh_3)_3]$ (X =Cl
or Br) or by passing Cl_2 gas in a solution of $[Rh(NS)(PPh_3)_3]$[91]
resulted in the formation of five coordinated species having a
general formula, $[Rh(NS)ClX(PPh_3)_2]$ (X =Cl or Br).[90] Their i.r.
spectra showed an absorption band in the region 1117-1120 cm^{-1}
assigned to ν_{NS}-. These are the few among the rather relatively
less known five coordinated complexes of rhodium in +3 oxidation
state.

Four Coordination

. Reaction of $(NSCl)_3$ with $Na[(\eta^5-C_5H_5)Cr(CO)_3]$ in THF resul-
ted in the formation of $[(\eta^5-C_5H_5)Cr(CO)_2(NS)]$[92] whose i.r.
spectrum showed three bands attributed to terminal CO and NS
groups. The crystal structure[92,93] exhibited its molecular geometry

to be the same as those of $[(\eta^5-C_5H_5)Mn(CO)_3]$[94] and $[(\eta^5-C_5H_5)-Cr(CO)_2(NO)]$[95] with bond lengths Cr-N, 1.694(3); Cr-C(O), 1.883(3); C-O, 1.131(3); N-S, 1.551(3) and bond angles Cr-N-S, 176.8(2)^0; Cr-C-O, 178.1(2)^0; C(O)-Cr-C(O), 92.4(2)^0; and C(O)-Cr-N, 94.8(1)^0. The bond lengths of Cr-C(Cp), Cr-C(O) and C-O are comparable to those found in other cyclopentadienyl chromium carbonyls.[95] The value of Cr-N-S angle (176.8(2)^0) suggested that NS ligand in the complex is essentially linked as NS^+. It was obvious on comparing the spectroscopic proper-ties of $[(\eta^5-C_5H_5)Cr(CO)_2(NO)]$ with its thionitrosyl analogue that the NS ligand is a better π-acceptor than NO.[95] Reactions of $[(\eta^5-C_5H_5)Cr(CO)_2(NS)]$ with NOCl and $NOPF_6$ yielded nitrosyl complex, $[(\eta^5-C_5H_5)Cr(NO)_2Cl]$ and nitrosyl-thionitrosyl complex, $[(\eta^5-C_5H_5)Cr(CO)(NS)(NO)]PF_6$ respectively.[93]

Nitrosyl Complexes

Bonding Modes of Nitric Oxide in Transition Metal Complexes

Nitrosyl group in transition metal complexes is generally considered to be bonded through nitrogen. Although substan-tial evidence have accumulated for metal-nitrogen coordination, there are still a few cases where there exists a possibility of linkage of metal atom through oxygen.[97] Three principle bonding modes in nitrosyl complexes are as follows:

I. Linear Complexes (M-N̂-O bond angle 175-180 degrees)

Complexes in group I are characterized by (i) linear M-N-O linkage, (ii) short M-N bond lengths and (iii) little or no trans influence of the NO group. In these complexes, NO group acts as an electron donor (Lewis base) towards transition metals and is formally considered to be coordinated as NO^+. The nitrogen atom is sp-hybridized, donating its lone-pair of electrons to the metal and accepting electrons into its unoccupied π^* orbitals from the occupied metal d orbitals. Energy level diagrams for {RuNO} complexes[99-101] are given in Fig. I.2. The multiple bond character of the M-N bond is in agreement with the observed short M-N distances.

II. Bent Complexes (M-N̂-O bond angle 120-125 degrees)

The characteristics of group III nitrosyl complexes are strikingly different from those of group I. Group III complexes have (i) M-N̂-O bond angle near 120 degrees, (ii) longer M-N bond lengths and (iii) a large trans influence of NO group. Here nitrosyl group is acting as a σ-electron acceptor (Lewis acid) and is formally considered to be coordinated as NO^-. M-N̂-O angle of 120 degrees would be anticipated since N atom is sp^2 hybridized.

III. Intermediate Complexes (M-N̂-O bond angle 125-175 degrees)

The complexes in group II have M-N-O angles that are significantly different from 180 and 120 degrees. Several reasons have been put forward for the observed bond angles

and in general the subject is still not well understood. A typical example of such complexes is $[RuI(CO)((C_6H_5)_3P)_2(NO)]$, where Ru-NO bond angle was found to be $159(2)^0$. This behaviour was explained on the basis of its highly distorted TBP geometry.[110]

M-$\widehat{N}$-O bond angles of all the nitrosyl complexes with known structures lie in the range $120-180^0$. Table I.1 presents a list of linear and bent nitrosyl complexes of ruthenium with various structural parameters.

Eight rules have been formulated by Ibers[112] for predicting the geometry of nitrosyl complexes. These are,

i) Without the assistance of special ligands first row transition metals usually do not have enough reducing power by themselves to bend the nitrosyl ligand; second row metals often do,and third row metals usually do.

ii) The number and size of bulky ligands play an important role; they usually go in the least sterically hindered positions: with one such ligand present, it usually occupies the nonaxial position. With two present, both are usually trans to each other and occupy the axial sites in TBP and nonaxial sites in SP. With three present, the SP geometry is usually not found, and all three would occupy the nonaxial sites in TBP.

iii) Strong π-acceptor ligands such as CO and NO (linear) and also σ-donor ligands with large trans effects, such as H and NO (bent), prefer not to be trans to each other in any

Table I.1: Structural parameters for {RuNO}^{6} (six coordinated) and {RuNO}^{8} (five coordinated) complexes

Complex	r(Ru-N) (Å)	r(N-O) (Å)	Ru-N-O (°)	Comments	Ref.
[RuOH(NH$_3$)$_4$(NO)]Cl$_2$	1.735(3)	1.159(5)	173.8(3)	Octahedral	102
(NH$_4$)$_2$[RuCl$_5$(NO)]	1.738(2)	1.131(3)	176.7(5)	Octahedral	102
K$_2$[RuCl$_5$(NO)]	1.747(6)	1.112(7)	176.8(9)	Octahedral	103
[RuCl$_3$(CH$_3$(C$_6$H$_5$)$_2$P)$_2$(NO)]	1.744(6)	1.132(6)	176.4(6)	Octahedral	104
[RuCl$_3$((C$_6$H$_5$)$_3$P)$_2$(NO)]	1.737(7)	1.142(8)	180.0(0)	Octahedral	105
[Ru(S$_2$CN(C$_2$H$_5$)$_2$)$_3$(NO)]	1.720	1.170	170.0	Octahedral	106
[RuBr$_3$((C$_2$H$_5$)$_2$SO)(NO)]$_2$	1.710(2)	1.160(1)	178.0(1)	Octahedral	107
[Ru(diphos)$_2$(NO)](BPh$_4$),(CH$_3$)$_2$CO	1.740(1)	1.200(1)	174.0(1)	TBP	108
[RuH((C$_6$H$_5$)$_3$P)$_3$(NO)]	1.792(11)	1.183(11)	176.0(1)	TBP	109
[RuI(CO)((C$_6$H$_5$)$_3$P)$_2$(NO)]	1.800(4)	1.150(5)	159.0(2)	TBP with severe distortion	110
[RuCl((C$_6$H$_5$)$_3$P)$_2$(NO)$_2$](PF$_6$),C$_6$H$_6$	1.743(20)	1.158(19)	178.0(2)	Distorted sp	111
	1.853(19)	1.662(20)	138.0(2)		

combination, if possible.

iv) Re and probably W and Mo, that form strong metal nitrogen multiple bonds and prefer ligands that are good π-acceptors, retard the bending of the attached nitrosyl group.

v) Bidentate ligands such as tetramethylethylenediamine, 1,10-phenanthroline, 2,2'-bipyridine, o-phenylenebis(dimethylarsine) and 1,2-bis(diphenylphosphine)ethane usually favour TBP geometry.

vi) Special multidentate ligands can promote one geometry over another, $HC(CH_2PPh_2)_3$ stabilizes the TBP geometry while tetraphenylporphyrin stabilizes the SP geometry.

vii) Ligands, that deactivate the metal by removing electron density from it and thereby decreasing its reducing power, favour the TBP geometry and the converse is also true.

viii) If the integrity of the nitrosyl ligand is maintained, all 20 electron systems must have bent nitrosyls. All six coordinate 18- and 17-electron nitrosyl complexes have linear nitrosyl ligands. Six coordinate 19-electron systems probably have partially bent NO ligands with M-$\widehat{N}$-O angles distinctly larger than 120°. All 16-electron systems have linear nitrosyl ligands.

Ibers,[105] after examining several hundred nitrosyl complexes has, however, proposed a set of rules relating the position of ν_{NO} and the mode of bonding in the complexes.

Attempts have also been made[113,114] to assign bent or linear M-NO structures on the basis of $\Delta\nu$ (difference between $\nu_{15_{NO}}$ and $\nu_{14_{NO}}$). The values of $\Delta\nu$ for complexes containing linear nitrosyl and those having bent structure lie in between 36 to 44 cm^{-1} and 25 to 28 cm^{-1} respectively. The value of ν_{NO} for nitrosyl group bridging between two metal atoms[115,116] occurs around 1500 cm^{-1} or slightly below. The coordinated hyponitrite, $N_2O_2^{2-}$ absorbs around 1185 cm^{-1}, 1045 cm^{-1} and 930 cm^{-1}.[117-119]

General Chemistry of Ruthenium Nitrosyls

Several reviews on the general chemistry of nitrosyls are available in the literature.[1-14,120,121] Some important aspects pertaining to the chemistry of $\{RuNO\}^6$, $\{RuNO\}^7$, $\{RuNO\}^8$ and $\{RuNO\}^{10}$ have been summarized in the following paragraphs:

$\{RuNO\}^6$ complexes:

$\{RuNO\}^6$ complexes so far synthesized are mononitrosyl, six coordinated with essentially linear Ru-N-O group. Table I.1 gives structural details of a few complexes illustrating these generalizations. Molecular orbital theory indicates that in six-coordinated, linear $\{RuNO\}^6$ complexes $d_{xz}(Ru) + \pi^*(NO)$, $d_{yz}(Ru) + \pi^*(NO)$ and $d_{xy}(Ru)$ orbitals should be the filled ones (Fig. I-2), with antibonding $d_{z^2}(Ru)-n(NO)$, $d_{yz}(Ru)-\pi^*(NO)$, $d_{xz}(Ru)-\pi^*(NO)$ and $d_{x^2-y^2}(Ru)$ orbitals empty.[8,98-101,122-124] As with the simple $Ru(II)-NO^+$ approach,
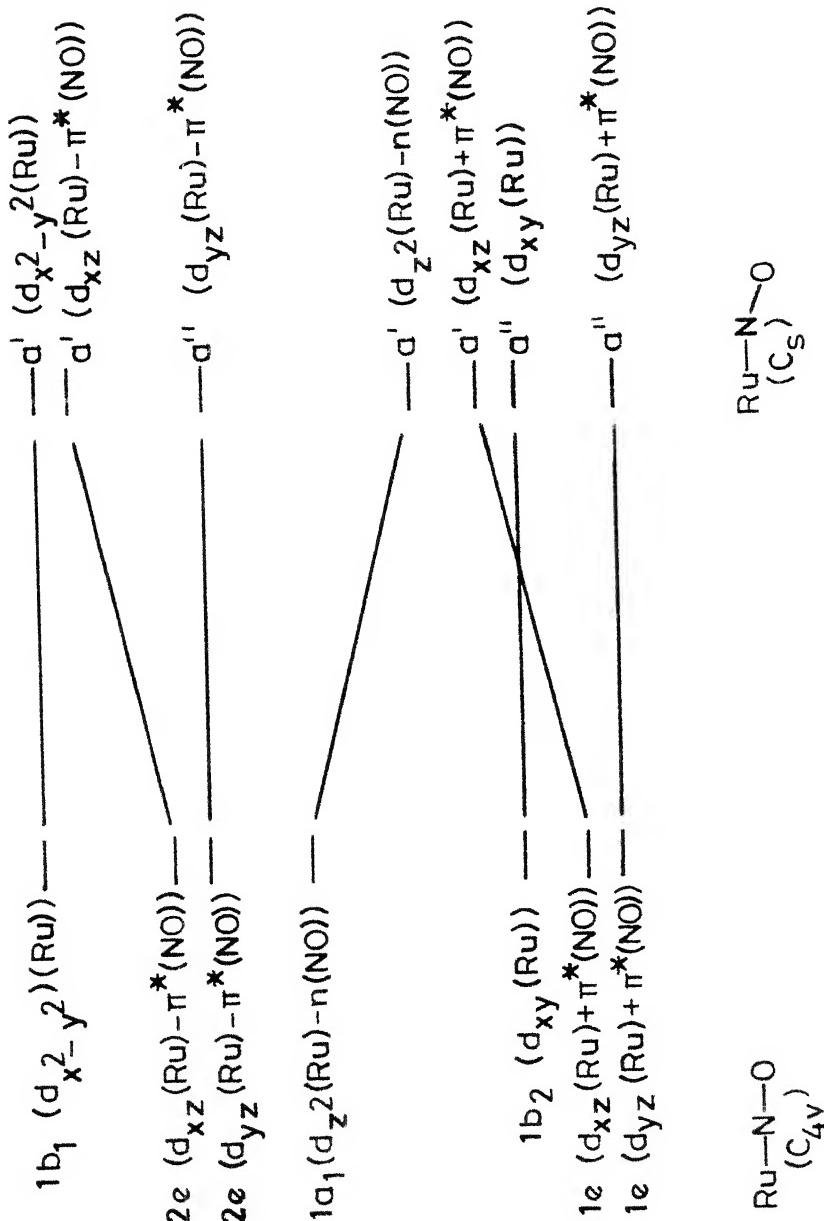
Fig.1.2 Energy level diagram for linear and bent {RuNO} complexes.

$1b_1$ $(d_{x^2-y^2})(Ru))$ ——————— a' $(d_{x^2-y^2}(Ru))$

$2e$ $(d_{xz}(Ru)-\pi^*(NO))$ ——————— a' $(d_{xz}(Ru)-\pi^*(NO))$

$2e$ $(d_{yz}(Ru)-\pi^*(NO))$ ——————— a'' $(d_{yz}(Ru)-\pi^*(NO))$

$1a_1(d_{z^2}(Ru)-n(NO))$ ——————— a' $(d_{z^2}(Ru)-n(NO))$

$1b_2$ $(d_{xy}(Ru))$ ——————— a' $(d_{xz}(Ru)+\pi^*(NO))$

$1e$ $(d_{xz}(Ru)+\pi^*(NO))$ ——————— a'' $(d_{xy}(Ru))$

$1e$ $(d_{yz}(Ru)+\pi^*(NO))$ ——————— a'' $(d_{yz}(Ru)+\pi^*(NO))$

Ru—N—O
(C_{4v})

Ru—N—O
(C_s)

potential electrophilic behaviour at N and nucleophilic at O
are anticipated. Despite the success of molecular orbital
theory in explaining and correlating the M-NO angle with the
electronic state of the complex, it is difficult to predict the
structures and reactivities of nitrosyls, which can be easily
predicted from their vibrational spectral studies than any
other technique. Haymore, et al. have concluded that the correc-
ted frequency, ν°_{NO} of linear nitrosyls {RuNO}[6] will be greater
than 1620 cm^{-1} as compared with that of bent nitrosyls which
will be less than 1610 cm^{-1}.[105,125-127]

The technically difficult method of [99]Ru Mössbauer
spectroscopy has been applied to provide information on the
bonding in {RuNO}[6] complexes. Investigations $[Ru(NH_3)_5(NO)]^{3+}$,
$[Ru(CN)_5(NO)]^{2-}$, $[RuCl_5(NO)]^{2-}$, $[Ru(NCS)_5(NO)]^{2-}$, $[RuBr_5(NO)]^{2-}$
and trans-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ [128-132] have indicated negative
isomer shift when a ligand in $[RuX_6]^{n+}$ is replaced by NO,
which suggested increased S-electron density on ruthenium
atom.

Although the studies by ESCA of N1s and O1s binding
energies provided useful information about the electron density
in the {MNO}group, because of the difficulties in sample pre-
paration, and relatively less studies made on these complexes
by this technique, the latter is unlikely to supplement the
simple i.r. method of deciding between linear and bent
nitrosyls. All the complexes studied including {RuNO}[6]

system have N1s binding energies close to 400 eV[133] and these
studies further suggested that the difference between N1s and
O1s binding energies of the bonded NO group can be used to
distinguish between linear $[(N1s)-(O1s) \approx 132$ eV $]$ and bent
$[(N1s)-(O1s) \approx 129$ eV$]$ groups.[134]

The important reactions of coordinated nitrosyl group
have been reviewed by McCleverty.[14] A new monoglycinato
nitrosyl complex of ruthenium(II), $K[Ru(gly)(OH)_3(NO)]$ was
isolated by the use of ion exchange resin from the products
formed as a result of the reaction between $[RuCl_3(H_2O)(NO)]$
and glycine.[135] The synthetic route for obtaining novel
dinuclear nitrosyl ruthenium(II) complexes $[RuX_2(NO)(R(EtO)PO)-$
$(R(EtO)POH)]_2$, (X = Cl or Br; R = OEt or OPh) by refluxing
$RuCl_3 \cdot xH_2O$ or $RuBr_3 \cdot xH_2O$, $p-MeC_6H_4SO_2NMe(NO)$ and excess of
$(EtO)_3P$ in dry EtOH[136,137] was explained through the forma-
tion of an intermediate $[Ru(NO)Cl_3(P(OEt)_3)_2]$. Substitution
reactions of $[RuCl_3(NO)L_2]$ (L = $AsPh_3$ or $SbPh_3$) have been
reported with different ligands[138] which proceeded via disso-
ciation mechanism with the formation of an intermediate,
$[RuCl_3(NO)L]$. Kinetics and mechanism of the anchoring of
$[RuCl_3(NO)(SbPh_3)_2]$ to polymer bound phosphinic ligands have
been studied.[29] The structure of $[Ru(NO)(Et_2SO)Br_3]_2$
obtained[139] from $[Ru(NO)L_2Br_3]$ (L = dialkyl or aryl-alkyl
sulfide or selenide) in diethylsulfoxide, has been determined
crystallographically.[107] Reactions of $[RuCl_2(PPh_3)_3]$ with
$[Co(NO)(DMGH)_2(MeOH)]$ yielded $[Ru(NO)Cl_3(PPh_3)_2]$ and

$[Ru(NO)_2(PPh_3)_2]$.[140,141]
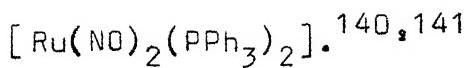
$[Ru(NO)(NH_3)_4Cl]Cl_2$ was obtained by the chlorination of $[Ru(NH_3)_6]Cl_2$.[142] The chloride bonded directly to metal was metathetically exchanged by acetate and cyanate ions. Nitrosyl group in $[Ru(NO)(NH_3)_5]X_3$ (X = Cl, Br or I) can be reduced to N_2O by reacting with hydroxylamine to form $[Ru(N_2O)(NH_3)_5]X_2$ from which N_2O can further be eliminated by its oxidation with Ce(IV).[143]

The aqueous solutions of $[Ru(NO)X_5]^{2-}$ (X = Cl, Br or I) at pH 0 $\rightarrow$ 14 with or without oxygen have been photolyzed[144] to $[Ru(H_2O)X_5]^{2-}$ and NO. $[Ru(NO)Cl_5]^{2-}$ reacted with barbituric acid (H_2L) to yield[145] $[Ru(NO)(LH)_2Cl_3]^{2-}$ and $[Ru(NO)(LH)_5]^{2-}$ $[Ru(NO)(AsPh_3)(Ph_3AsO)Cl_3]$ has been synthesized by passing NO through $[Ru(AsPh_3)_2(Ph_3AsO)Cl_3]$.[146] Reaction of $[Ru(NO)(bipy)_2X]^{2+}$ (X = Cl or NO_2) with PhNRMe (R = H or Me) produced[147] $[Ru(bipy)_2 \{N(=O)C_6H_4NRMe\}X]^+$ ion.

A series of new dithiocarbamato complexes,[148] trans-$[Ru(NO)(S_2CNRR')_2Cl]$ (R = R' = Me, Et; R = Me, R' = Et; R = Me, R' = Ph), trans-$[Ru(NO)(S_2CNMe_2)_2OH]$.MeOH, trans-$[Ru(NO)-(S_2CNMe_2)_2(H_2O)][BF_4]$, trans-$[Ru(NO)(S_2CNMe_2)_2.MeOH][PF_6]$, cis-$[Ru(NO)(S_2CNMe_2)_2X]$ (X = F, Br, I, NO_2) have been reported. Nitrosylation of $[Ru(CN)_6]^{4-}$ with HNO_3 resulted in the formation of $[Ru(NO)(CN)_3(H_2O)_2]$.[149] The synthesis of potassium salt of $[Ru(OCH_2CO_2)_2(OH)(NO)]$ has been carried out by reacting $[RuCl_3(H_2O)_2(NO)]$ with glycolic acid. A review discussing the

contribution of polarography to some problems of reactivity and structure of nitrosyl complexes has recently appeared.[150]

{RuNO}[7] Complexes

The synthetic route to obtain complexes of {RuNO}[7] system is through one electron reduction of {RuNO}[6] complexes. Thus, $[RuX(bipy)_2(NO)]^{n+}$ (X = Cl^-, N_3^- for n = 2; X = pyridine, CH_3CN or NH_3 for n = 3) have been reversibly reduced chemically (I^-) or electrolytically to give the corresponding {RuNO}[7], $[RuX(bipy)_2(NO)]^{(n-1)+}$ complexes of which $[RuCl(bipy)_2NO]I$ and $[Ru(CH_3CN)(bipy)_2(NO)][PF_6]$ were isolated as solids.[32,33,120] The interesting part of this work has been that while all physical measurements (i.r., e.s.r., ESCA, Mossbauer, electronic spectroscopy and electrochemistry) indicated extensive $d\pi(Ru)$-$\pi^*(NO)$ overlap in {RuNO}[7] complexes, they at the same time also indicated that the added electron entered a molecular orbital, mainly located on NO ligand which must be $d_{xz}(Ru)$-$\pi^*(NO)$ or $d_{yz}(Ru)$-$\pi^*(NO)$ antibonding orbital (Fig. I.2) which should therefore result in significant bending of {RuNO} group.

{RuNO}[8] Complexes

If two electrons are added to {RuNO}[6] to form {RuNO}[8] complexes, they should occupy either d_{z^2}-n(NO) or d_{xz}-$\pi^*(NO)$ antibonding orbital[98] (M.O. diagram, Fig. I.2). The consequences of which will be: (1) bending will be strongly favoured in case of six coordinated {RuNO}[8] complexes[8,101,122]

and (2) if the complexes formed are five coordinated (more likely, since $d_{z^2}(Ru)-n(NO)$ is stabilized by the loss of the sixth ligand)[8] TBP geometry will be associated with linear NO and SP, with bent NO. Some of the rules for predicting the geometry of pentacoordinate {RuNO}[8] complexes have been given by Haymore and Ibers.[99,101,112] The important reactions of {RuNO}[8] complexes have been reviewed by Bottomley.[13] One of the important {RuNO}[8] complexes, $[RuCl(PPh_3)_2(NO)]$ reacted with a number of reagents, e.g., acidchlorides, alkynes, olefin, o-quinone, 1,2-benzoquinone, 9,10-phenanthroline, tosylchloride, HCl, CO, SO_2, O_2, etc. to produce six coordinated products.[13] The reaction of $[Ru(\eta^5-C_5H_5)(PMe_3)_2Cl]$ with $NOPF_6$ gave $[Ru(\eta^5-C_5H_5)(PMe_3)_2(NO)][PF_6]$.[151]

$[Ru(NO)(A)_2]^+$ (A = DPE, $Ph_2PCH_2CH_2PPh_2$ or DPP, $Ph_2PCH_2CH_2CH_2PPh_2$) have been electrochemically reduced to form {RuNO}[9] and {RuNO}[10] complexes. $[Ru(NO)(DPE)_2]^+$ ({RuNO}[8]; ν_{NO}, 1677 cm^{-1}) produced $[Ru(NO)(DPE)_2]$ ({RuNO}[9]; ν_{NO}, 1432 cm^{-1}) and $[Ru(NO)(DPE)_2]^-$ ({RuNO}[10]; ν_{NO}, 1430 cm^{-1}) in two one-electron reductions.[152,153] In this system of reduction from {RuNO}[8] to {RuNO}[10], the difference in frequencies of ν_{NO} was found to be 250 cm^{-1} which is of the same order as that when free NO^+ is reduced to NO.[11] A phosphine molecule in trans-$[RuCl(NO)(PPh_3)_2]$ was exchanged[154] by 2,11-bis(diphenylphosphinomethyl)benzophenanthrene (L-L) to produce trans-$[RuCl(NO)(L-L)]$ which in turn gave $[RuCl(CO)(NO)(L-L)]$ on reaction with CO in benzene.

{RuNO}[10] Complexes

Only a few examples of {RuNO}[10] system are known. The complex, $[Ru(NO)_2(PPh_3)_2]$ prepared by several workers,[107,155,156] has been found to be extremely reactive and to undergo substitution and NO transfer reactions.[13] The product of its reaction with SO_2,[159] $[Ru(NO)_2(PPh_3)_2(SO_2)]$ readily oxidized to the corresponding sulfato complex. Hoffmann, et al.[158] reviewed the factors which influenced the geometries and structures of tetrahedral, planar and related dimeric nitrosyl species like $[Ru(NO)_2(PPh_3)_2]$ and $[Ru(NO)(PPh_3)(\mu-PPh_2)]_2$. $[Ru(\eta^3-C_3H_5)(PPh_3)_2(NO)]$, another example of {RuNO}[10] system[31] has been synthesized. X-ray data of $[Ru(NO)_2(PPh_3)_2]$ showed its geometry to be distorted tetrahedral with linear Ru-NO groups.[157]

Bridging and Cluster {RuNO} Complexes

$[Ru_3(CO)_{10}(NO)_2]$ the only well characterised NO bridged complex was obtained from $[Ru_3(CO)_{12}]$ and NO.[160] Until now, only three nitrosyl cluster complexes of ruthenium $Ru_2(\mu-PPh_2)_2(PPh_3)_2)(NO)_2]$, $[Ru_4(\mu-PPh_2)_4(\mu-Cl_4)(NO)_4]$ and $[Ru_3(CO)_7H(NO)(P(OMe)_3)_3]$[161-163] have been synthesized.

Nitro, Nitrato Complexes of Ruthenium, Palladium and Platinum

Notwithstanding a considerable advance in transition metal nitrite, nitrate chemistry in 1960 s,[164] great majority

of platinum metal nitro and nitrato complexes that had been
identified towards the end of the decade, were largely of the
'classical' type in which nitro or nitrato group behaved as a
hard Lewis base.[165] In recent years, however, a number of
platinum metal nitro and nitrato complexes have been synthe-
sized in which central metal was present in a low oxidation
state. All the work until 1978 concerning such complexes have
been reviewed by Critchlow.[166] A brief uptodate survey of
nitro and nitrato complexes of ruthenium, palladium and platinum
is given in the following paragraphs:

Nitro complexes of bis(bipyridine)ruthenium(III) have
been found to be unstable with respect to oxidation of the
coordinated nitroligand. For complexes, $[Ru(bipy)_2L(NO_2)]^+$
(L = NH_3, pyrazine, CH_3CN, PPh_3) and $[Ru(bipy)_2Cl(NO_2)]$,
electrochemical oxidation to the Ru(III) resulted in the
formation of corresponding nitrosyl and nitrato complexes in
1 : 1   ratio.[167] Coordinated carbon monoxide in $[Ru(NO)_2(CO)_2-$
$(PPh_3)_2]$ was converted into carbon dioxide via oxygen transfer
from coordinated nitrite.[179] Palladium nitrosyl acetate
complex $[Pd_2(NO)(CH_3COO)_3]_2 \cdot CH_2Cl_2$ has been prepared[168] and
its structure has been determined. Palladium nitro-nitrosyl
couple catalyse the oxidation of olefin to ketones.[169] cis-
$[Ru(NO)(NO_2)(S_2CNMe_2)_2]$ has been prepared by Feltham, et al.[148]
The alkylation of NO group to form $[Ru(bipy)_2(Py)(N(O)OR)]^{2+}$
(R = Me, Et, Bu, iso-Pr) was carried out by reactions involving
attack of the corresponding alkoxide ions[170] on the nitrosyl

N-atom in $[Ru(bipy)_2(Py)(NO)]^{3+}$. Oxidation of the ligand in nitro complexes of ruthenium(III) has been studied.[167] The reaction of SO_2 with $[Pt(N_2O_2)(PPh_3)_2]$ and NO with $[Pt(PPh_3)_3\text{-}SO_2]$ resulted in the formation of $[Pt(NO_2)_2(PPh_3)_2]$ and $[Pt(PPh_3)_3(SO_3)]$, respectively. Both these reactions have arisen from ready oxygen transfer reaction. $[Pt(N_2O_2)(PPh_3)_2(SO_2)]$ has been prepared and formulated as an insertion product on the basis of i.r. and chemical studies.[159] Bhaduri, et al. studied in detail the reactions of carbon monoxide with trans-$[M(NO_2)_2L_2]$ (M = Pd; L = PEt_2Ph, PEt_3; M = Pt; L = PEt_2Ph, PEt_3, PBu_3). The palladium and platinum complexes gave $[M(CO)_2L_2]$ and subsequently higher clusters like $[M_3(CO)_3L_4]$, except for $[Pt(PEt_3)_2(NO_2)_2]$ in which case $[Pt(NO)(NO_2)(PEt_3)_2]$ and $[Pt(NCO)(NO_2)(PEt_3)_2]$ have been isolated. $[Pt(NO)(NO_3)(PPh_3)_2$ was prepared by the reaction of N_2O_4 with $Pt(PPh_3)_4$ in toluene. $[Pt(NO)(NO_3)(PPh_3)_2]$ reacted with O_2 to give trans-$[Pt(NO_3)_2(PPh_3)_2]$.[36]

Palladium and Platinum Nitrato Complexes as Catalyst

The insertion of an olefin into a metal-hydride bond is thought to be one of the key steps in the catalytic addition of hydrogen to an unsaturated bond. The insertion of ethylene into platinum-hydrogen bond was first noted in the case of trans-$[PtHCl(PEt_3)_2]$ by Chatt,[171] yielding trans-$[Pt(C_2H_5)Cl(PEt_3)_2]$ under relatively extreme conditions (368 K, 40 atmospheres). On substituting chloride by nitrate, it has been

found that the ease of insertion could be considerably

increased. For example, trans-$[PtH(NO_3)(PPh_2Me)_2]$

formed trans-$[Pt(C_2H_5)(NO_3)(PPh_2Me)_2]$[172,173] at room temperature.

Trans-$[PtH(NO_3)(PPh_2Me)_2]$ catalyzed controlled oxidation of

$(CH_2=CHCH_2)_2O$ to propaldehyde[174] $[Pd(MeCO_2)(NO_3)(2,2'-bipyri-$

dyl)] has been found to catalyse the acetoxylation of chloro-

benzene.[175] Palladium(II) nitrate and PPh_3 in the molar ratio

1:3 have been shown to catalyse the reactions of Schiff bases

with 1,3-butadiene to yield a vinyl-substituted piperidine,[35]

while in acetic acid solution the same system[34] in the molar

ratio 1:1, catalysed allene polymerization.

Cyclic Voltammetric Studies

Electrochemical behaviour of nitrogen oxides have been

studied by a number of workers in different solvents[37-42] but

those of the thio-analogues have not yet been taken up.

Although a few reports are available on the electrochemical

behaviour of S_4N_4,[176-178] no report is available for tri-

thiazyltrichloride.

REFERENCES

1. W.P. Griffith, The Chemistry of Rarer Platinum Metals, Interscience, London (1967).

2. B.F.G. Johnson and J.A. McCleverty, Progr. Inorg. Chem., 7, 277 (1966).

3. N.G. Connelly, Inorg. Chim. Acta Rev., 6, 48 (1972).

4. J.A. McGinnety, M.T.P. Int. Rev. Sci. Inorg. Chem., Ser. One, 5, 229 (1972).

5. K.G. Caulton, Coord. Chem. Rev., 14, 317 (1975).

6. W.P. Griffith, Advan. Organomet. Chem., 7, 211 (1968).

7. J. Masek, Inorg. Chim. Acta Rev., 3, 99 (1969).

8. J.H. Enemark and R.D. Feltham , Coord. Chem. Rev., 13, 339 (1974).

9. F. Bottomley, Accounts Chem. Res., 11, 158 (1978).

10. B.A. Frenz and J.A. Ibers, M.T.P. Int. Rev. Sci., Phys. Chem., Ser. One, 11, 33 (1972).

11. J.H. Swinehart, Coord. Chem. Rev., 2, 385 (1967).

12. R. Eisenberg and C.D. Meyer, Accounts Chem. Res., 8, 26 (1975).

13. F. Bottomley, Coord. Chem. Rev., 26, 7 (1978).

14. J.A. McCleverty, Chem. Rev., 79, 56 (1979).

15. J. Chatt and J.R.Dilworth, J. Chem. Soc.,Chem. Comm., 508 (1974).

16. M.W. Bishop, J. Chatt and J.R. Dilworth, J. Chem. Soc., Chem. Comm., 780 (1975).

17. M.W. Bishop, J. Chatt and J.R. Dilworth, J. Chem. Soc., Dalton Trans., 1, 1 (1979).

18. B.W.S. Kolthamer, P. Legzdins, J. Am. Chem. Soc., 100, 2247 (1978).

19. K.K. Pandey and U.C. Agarwala, Z. Anorg. Allgem. Chem., 461(2), 231 (1980).

20. K.K. Pandey, S. Datta and U.C. Agarwala, Z. Anorg. Allgem. Chem., 468, 228 (1980).

21. K.C. Jain, K.K. Pandey, S.S. Katiyar and U.C. Agarwala, XXI Internat. Conf. Coord. Chem., France, 440 (1980).

22. K.K. Pandey and U.C. Agarwala, Inorg. Chem., 20(4), 1308 (1981).

23. K.K. Pandey, K.C. Jain and U.C. Agarwala, Inorg. Chim. Acta, 48, 23 (1981).

24 B.F.G. Johnson and S. Bhaduri, J. Chem. Soc., Chem. Comm., 650 (1973).

25. B.L. Haymore and J.A. Ibers, J. Am. Chem. Soc., 96, 3325 (1974).

26. S. Bhaduri, B.F.G. Johnson, C.J. Savory, J.A. Segal, and R.H. Walter, J. Chem. Soc., Chem. Comm., 809 (1974).

27. S. Bhaduri and B.F.G. Johnson, Trans. Met. Chem., 3, 156 (1978).

28. J. Reed and R. Eisenberg, Science, 184, 568 (1974).

29. G. Innorta, A. Modelli, F. Scagnolari, F.A. Francesco, J. Org. Met. Chem., 186(2), 271 (1980).

30. J.A. McCleverty, C.W. Ninnes and I. Wojochowicz, J. Chem. Soc., Chem. Comm., 1061 (1976).

31. M.W. Schoonover and R. Eisenberg, J. Am. Chem. Soc., 99, 8371 (1977).

32. R.W. Callahan and T.J. Meyer, Inorg. Chem., 16, 574 (1977).

33. R.W. Callahan, G.M. Brown and T.J. Meyer, J. Am. Chem. Soc., 97, 894 (1975).

34. G.D. Sheir, J. Org. Met. Chem., 10, P15 (1967).

35. J. Furukawa, J. Kiji, H. Tomita and K. Yamamoto, Chem. Comm., 506 (1974).

36. S. Bhaduri, B.F. Johnson, F.G. Brian, A. Khair, J.A. Segal, Walters Roberts and Zuccaro, Camillo, J. Chem. Soc. Dalton Trans., 1, 234 (1981).

37. J.B. Headridge and D. Pletcher, J. Polarogr. Soc., 13, 167 (1967).

38. G. Bianchi, T. Mussini and C. Traini, Chim. Ind. (Milan), 45, 1333 (1963).

39. P.G. McCormic and H.S. Swofford Jr., Anal. Chem., 41, 146 (1969).

40. C. Tamayo Garcia, A.J. Calandra and A.J. Arvia, Electrochim. Acta, 17, 2181 (1972).

41. A.J. Calandra, C. Tamayo, J. Herrera and A.J. Arvia, Electrochim. Acta, 17, 2035 (1972).

42. B. Gino, M.G. Antonio and M. Franco, Electroanal. Chem. and Interf. Electrochem., 55, 91 (1974).

43. W. Clay, O. Glemser, K. Harms, G. Hastmann, R. Mews, M. Noltemeyer, G. Sheldrik, Acta Crystallograph., B 37(3), 548 (1981).

44. K.K. Pandey, D.K.M. Raju, H.L. Nigam and U.C. Agarwala, Proc. Ind. National Sci. Acad. (in press).

45. H.G. Heal, Adv. Inorg. Chem. Radiochem., 15, 376 (1972).

46. K. Dressler, Helv. Phys. Acta, 28, 563 (1955).

47. A. Mandl, J. Chem. Phys., 54, 4129 (1971).

48. P.A.G. O'Hare, J. Chem. Phys., 52, 2992 (1970).

49. R. Byfleet, A. Carrington and D.K. Russel, Mol. Phys., 20, 271 (1971).

50. F. Torok, P. Pulay, T. Szondy and P. Nagy, Acta Chim., 80, 139 (1974).

51. N.A. Narasimhan, K. Raghubeer and T.K. Balasubramanian, J. Mol. Spectrosc., 54, 160 (1975).

52. F.J. Lovas, E. Jiemann, J. Phys. Chem., Ref. Data 3, 609 (1974).

53. H.R. Johnson, R.F. Beebe and C. Sneden, Astrophys. J. Suppl. Ser., 29, 123 (1975).

54. Chi-Lian Chiu, Diss. Abstr. Int., B36, 254 (1975).

55. C.A. Gottlieb, J.A. Ball, E.W. Gottieb, C.J.Lada and H. Penfield, Astrophys. J., 200, L-147 (1975).

56. T.B.H. Kuiper, B. Zuckerman, R.K. Kakar and E.R. Kuiper, Astro. Phys., J., 200, L-151 (1975).

57. A. Jenouvrier and D. Daumont, J. Mol. Spectros., 61, 313 (1976).

58. Chi-Lian Chiu and S.J. Silvers, J. Mol. Spectrosc., 61, 316 (1976).

59. M. Vervloet and A. Jenouvrier, Can. J. Phys., 54, 1909 (1976).

60. J.M. Dyne, A. Morris and I.R. Trickle, J. Chem. Soc., Faraday Trans., 73, 147 (1977).

61. Ringers A. Douglas, U.S. NTIS AD Rep. 1977, AD-A037802, p. 18.

62. D.A. Varshalovich and V.K. Khersonskii, Astron. Zh., 54, 915 (1977).

63. K. Raghuveer and N.A. Narasimhan, J. Mol. Spectrosc., 70, 323 (1978).

64. Z. Iqbal and D.S. Dowas, Proc. Int. Conf. Lattices Dyn., 582 (1977).

65. Murai Hisao, Yagi Toshikiko, Obi Kinichi and Tanaka Ikuzo, Chem. Phys. Lett., 61, 513 (1979).

66. R.A. Teichman and R.E. Nixon, Inorg. Chem., 15, 1993 (1976).

67. R.F. Barrow, G. Drummoud and P.B. Zuman, Proc. Phys. Soc., A 67, 365 (1954).

68. D. Chapman, R.J. Warm, R.G. Fitygerald and B.D. Fyoffe, Trans. Faraday Soc., 60, 294 (1964).

69. G. Nickless, Inorganic Sulphur Chemistry, Elsevier, N.Ẏ. (1968).

70. O. Glemser and W. Koch, Angew. Chem. Int. Ed., 10, 127 (1971).

71. O. Glemser and W. Koch, Ann. Asoc. Guim. Argen., 59, 143 (1971).

72. O. Glemser and H. Richert, Z. Anorg. Allgem. Chem., 307, 313 (1961).

73. O. Glemser, H. Richert and H. Haeseler, Angew. Chem., 71, 524 (1959).

74. R. Mews, Angew. Chem. Int. Ed., 15, 691 (1976).

75. R. Mews, D.L. Wegener and O. Glemser, Z. Anorg. Allgem. Chem., 412, 148 (1975).

76. H. Richert and O. Glemser, Z. Anorg. Allgem. Chem., 307, 328 (1961).

77. O. Glemser, Angew. Chem. Int. Edn., 2, 530 (1963).

78. D. Chapman and T.C. Waddington, Trans. Faraday Soc., 58, 1679 (1962).

79. A.J. Banister, L.F. Moore and J.S. Padley, Spectrochim. Acta, Part A 23, 2705 (1967).

80. H. Garcli-Fernandez, C.R. Acad. Sci., C265, 88 (1967).

81. O. Glemser and H. Perl, Naturwisson, 48, 620 (1961).

82. W. Muthmann and E. Seitter, Chem. Ber., 30, 627 (1977).

83. A. Meuwsen, Chem. Ber., 2311 (1931).

84. R.L. Dekock and M.S. Haddad, Inorg. Chem., 16, 216 (1977).

85. M.W. Hursthouse and M. Motevalli, J. Chem. Soc. Dalton Trans., 1362 (1979).

86. T.F. Brennen and I. Bernal, Inorg. Chim. Acta, 7, 28 (1973).

87. K.K. Pandey, R.C. Srivastava and U.C. Agarwala (unpublished results) (1981).

88. K.W. Muir, L. Manojlovin-Muir and R. Herak (unpublished work).

89. K.K. Pandey and U.C. Agarwala, Indian J. Chem. 20A, SCCA 2077 (1981).

90. D.K.M. Raju, Thesis (M.Phil), Indian Institute of Technology, Kanpur, India (1980).

91. K.K. Pandey, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India (1980).

92. T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, J. Chem. Soc., Chem. Comm., 1036 (1978).

93. T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, Inorg. Chem., 18, 3548 (1979).

94. A.F. Berndt and R.E. Marsh, Acta Cryst., 16, 118 (1963).

95. J.L. Atwood, R. Shakir and J.T. Malito, J. Organomet. Chem., 165, 65 (1979).

96. R. Grinter and J.D. Woolins, Inorg. Chim. Acta, 39(2), 193 (1980).

97. R.J. Irving, Rec. Chem. Progr., 26, 115 (1965).

98. R. Hoffman , M.M-L.Chen and D.L. Thorn, Inorg. Chem.,
     16, 503 (1977).

99. D.M.P. Mingos, Inorg. Chem., 12, 1209 (1973).

100. C.G. Pierpont and R. Eisenberg, J. Am. Chem. Soc., 93,
     4905 (1971).

101. R. Hoffman , M.M-L.Chen, M. Elian, A.R. Rossi and D.M.P.
     Mingos, Inorg. Chem., 13, 2666 (1974).

102. F. Bottomley, J. Chem. Soc. Dalton Trans., 1600 (1974).

103. J.T. Veal and D.J. Hodgson, Inorg. Chem., 11, 1420 (1972).

104. A.J. Schultz, R.L. Henry, J.Reed and R. Eisenberg, Inorg.
     Chem., 13, 732 (1974).

105. B.L. Haymore and J.A. Ibers, Inorg. Chem., 14, 3060
     (1975).

106. A. Domenicano, A. Vaciago, L. Zambonelli, P.L. Loader
     and L.M. Venanzi, Chem. Comm., 476 (1966).

107. J.E. Fergusson, C.T. Page and W.T. Robinson, Inorg. Chem.,
     15, 2270 (1976).

108. C.G. Pierpont and R. Eisenberg. Inorg. Chem., 12, 1099
     (1973).

109. C.G. Pierpont and R. Eisenberg, Inorg. Chem.,11, 1094
     (1972).

110. D. Hall and R.B. Williamson, Cryst. Struct. Comm., 3,
     327 (1974).

111. C.G. Pierpont and R. Eisenberg, Inorg. Chem., 11, 1088
     (1972).

112. B.L. Haymore and J.A. Ibers, Inorg. Chem., 14, 2610
     (1975).

113. E. Miki, K. Mizumachi, T. Ishimon and H. Okuno, Bull.
     Chem. Soc. Japan, 46, 3779 (1973).

114. E. Miki, K. Mizumachi and T. Ishimon, Bull. Chem. Soc. Japan, _48_, 2975 (1975).

115. R.C. Elder, F.A. Cotton and R.A. Schunn, J. Am. Chem. Soc., _89_, 3645 (1967).

116. R.B. King and M.B. Bisnette, Inorg. Chem., _3_, 791 (1964).

117. E.E. Mercer, W.A. McAllister and R.R. Durig, Inorg. Chem., _6_, 1819 (1967).

118. R.D. Feltham and J.T. Corriol, Inorg. Chem., _3_, 1038 (1964).

119. R.D. Feltham, Inorg. Chem., _8_, 344 (1969).

120. F. Bottomley and F. Grein, J. Chem. Soc. Dalton Trans., _8_, 1359 (1980).

121. T.W. Hawkins and M.B. Hall, Inorg. Chem., _19_, 1735 (1980).

122. J.H. Enemark and R.D. Feltham, Proc. Nat. Acad. Sci., U.S.A., _69_, 3534 (1971).

123. R.F. Fenske and R.L. DeKock, Inorg. Chem., _11_, 437 (1972).

124. P.T. Manoharan and H.B. Gray, Inorg. Chem., _5_, 823 (1966).

125. A.P. Gaughan, B.L. Haymore, J.A. Ibers, W.H. Myers, T.F. Nappier and D.W. Meek, J. Am. Chem. Soc., _95_, 6859 (1973).

126. R.W. Adams, J. Chatt, N.E. Hopper and G.J. Leigh, J. Chem. Soc. Dalton Trans., 1075 (1974).

127. F. Bottomley and E.M.R. Kiremire, J. Chem. Soc. Dalton Trans., 1125 (1977).

128. D. Guenzburger, A. Garnier and J. Danon, Inorg. Chim. Acta, _21_, 119 (1977).

129. G.M. Bancroft, K.S. Butler and E.T. Libbey, J. Chem. Soc. Dalton Trans., 2643 (1972).

130. R. Greatrex, N.N. Greenwood and P. Kapsi, J. Chem. Soc. A, 1873 (1971).

131   R.A. Parados, C.A. Clausen and M.L. Good, J. Coord. Chem., 2, 201 (1973).

132.   W. Potzel, F.E. Wagner, U. Zahn, R.L. Mossbauer and J. Danon, Z. Phys., 240, 306 (1970).

133.   P. Finn and W.L. Jolly, Inorg. Chem., 11, 893 (1972).

134.   C.C. Su and J.W. Faller, J. Organomet. Chem., 84, 53 (1975).

135.   I. Toshio, M. Takashi, Bull. Chem. Soc. Japan, 52, 619 (1979).

136.   T.G. Southern, P.H. Dixneuf, J.Y. Le Marouille, D. Grandjean, Inorg. Chim. Act, 31, L415 (1978).

137.   T.G. Southern, P.H. Dixneuf, J.Y. Le Marouille and D. Grandjean, Inorg. Chem., 18, 2987 (1979).

138.   G. Innorta, A. Foffani, S. Torroni and G. Serrazanetti, Inorg. Chim. Acta, 35, 189 (1979).

139.   J.E. Fergusson and C.J. Page, Austral. J. Chem., 29, 2159 (1976).

140.   C.B. Ungermann and K.G. Caulton, J. Am. Chem. Soc., 98, 3862 (1976).

141.   S. Cenini, A. Mantovani, A. Fusi and M. Keubler, Gazz. Chim. Ital., 105, 255 (1975).

142.   A.F. Schreiner and S.W. Lin, Inorg. Synth., 16, 13 (1976).

143.   F. Bottomley, Inorg. Synth., 16, 75 (1976).

144.   A.B. Nikolskii, A.M. Popov and I.V. Vasilevskii, Koord. Khim., 2, 671 (1976).

145.   S. Sueur, C. Bremard and G. Nowogrocki, Bull. Soc. Chim. France, 1051 (1976).

146.   K. Natarajan, R.K. Poddar and U. Agarwala, Inorg. Nucl. Chem. Lett., 12, 749 (1976).

147. W.L. Bowden, W.F. Little and T.J. Meyer, J. Amer. Chem. Soc., 98, 444 (1976).

148. J.V. Dubrawski and R.D. Feltham, Inorg. Chem., 19, 355 (1980).

149. A.B. Nikolskii, A.M. Popov, N.B. Batalova, Koord. Khim., 5, 1851 (1979).

150. J. Masek, Chemicke listy Academia, 74(7), 751 (1980).

151. P.M. Treichel and D.A. Komar, Synth. React. Inorg. Metal Org. Chem., 10, 205 (1980).

152. G. Zotti, G. Pilloni, M. Bressan and M. Martelli, J. Electroanal. Chem., 75, 607 (1977).

153. G. Pilloni, G. Zotti and S. Zecchin, J. Electroanal. Chem., 125, 129 (1981).

154. R. Holderegger, L.M. Venanzi, F. Bachechi, P. Mura, L. Zambonelli, Helv. Chim. Acta, 62, 2159 (1979).

155. J.J. Levison and S.D. Robinson, Chem. Ind., 1514 (1969).

156. J.J. Levison and S.D. Robinson, J. Chem. Soc. A, 2947 (1970).

157. S. Bhaduri and G.M. Sheldrick, Acta Crystallogr. Sect. B, 31, 897 (1975).

158. R.H. Summerville and R. Hoffmann, J. Am. Chem. Soc., 98, 7240 (1976).

159. S. Bhaduri, B.F.G. Johnson, A. Khair, I. Chatak, D.M.P. Mingos, J. Chem. Soc. Dalton Trans., 9, 1572 (1980).

160. J.R. Norton, J.P. Collman, G. Dolcetti and W.T. Robinson, Inorg. Chem., 11, 382 (1972).

161. R. Eisenberg, A.P. Gaughan, C.G. Pierpont, J. Reed and A.J. Schultz, J. Am. Chem. Soc., 94, 6240 (1972).

162. J. Reed, A.J. Schultz, C.G. Pierpont and R. Eisenberg, Inorg. Chem., 12, 2949 (1973).

163. B.F.G. Johnson, P.R. Raithby and C. Zuccaro, J. Chem. Soc. Dalton Trans., 1, 99 (1980).

164. C.C. Addison and D. Sutton, Prog. Inorg. Chem., 8, 195 (1967).

165. R.G. Pearson, Chem. Brit., 3, 103 (1967).

166. P.B. Critchlow and S.D. Robinson, Coord. Chem. Rev., 25, 69 (1978).

167. F.R. Keene, D.J. Salmon, J.L. Walsh, H.D. Abruna, T.J. Meyer, Inorg. Chem., 19, 1896 (1980).

168. N.V. Podberezskaya, V.V. Bakakin, N.I. Kuznetsova, A.F. Damilyuk, V.A. Likholobov, Dokl. Akad. Nauk.SSSR, 256, 870 (1931).

169. M.A. Andrews and K.P. Kelly, J. Am. Chem. Soc., 103, 2394 (1981).

170. J.L. Walsh, R.M. Bullock, T.J. Meyer, Inorg. Chem., 19, 865 (1980).

171. J. Chatt and B.L. Shaw, J. Chem. Soc., 5075 (1962).

172. H.C. Clark and H. Kurosawa, Chem. Comm., 957 (1971).

173. H.C. Clark and H. Kurosawa, Inorg. Chem., 11, 1275 (1972).

174. H.C. Clark and H. Kurosawa, Inorg. Chem., 12, 1566 (1973).

175. L. Eberson and E. Jonsson, Acta Chem. Scand., Ser. B, 28, 771 (1974).

176. J.D. Williford, R.E. Van Reet, M.P. Eastman and K.B. Prater, J. Electrochem. Soc., 120, 1498 (1973).

177. O.R. Brown, J. Electroanal. Chem., 34, 419 (1972).

178. J.W. Tweh and A.G. Turner, Inorg. Chim. Acta, 48, 173 (1981).

179. D.T. Doughty, R.P. Stewart, Jr., Gilbert Gordon, J. Am. Chem. Soc., 103, 3388 (1981).

INTERACTION OF TRITHIAZYLTRICHLORIDE
WITH RUTHENIUM COMPLEXES

During the past few years there has been an upsurge in
the study of transition metal nitrosyl complexes[1-4] and their
reactions.[5,6] Although the literature is replete with such
studies, the work on their thioanalogues is practically in rudi-
mentary state possibly owing to the lack of a suitable thioni-
trosylating agent. A few thionitrosyl complexes which are known
until recently, have been synthesized either by the reactions
of elemental sulfur, propylene sulfide or disulfurdichloride
with coordinated nitrido ligands[7-9] or by the reactions of
trithiazyltrichloride with $Na[(\eta^5-C_5H_5)Cr(CO)_3]$[10] and with
ruthenium, osmium, rhodium and iridium ions or complexes in
presence of triphenylphosphine and triphenylarsine in tetrahy-
drofuran.[11,15,16] X-ray studies of $[(\eta^5-C_5H_5)Cr(CO)_2NS]$[12,13]
and $[Mo(NS)(S_2CNMe_2)_3]$[14] have indicated the mode of bonding
of thionitrosyl group as terminal, linear NS^+ with M-$\widehat{N}$-S angle
$176.8(2)^0$ and $172.0(7)^0$ respectively. No report has, however,
appeared of a complex with two NS or one nitrosyl and one

thionitrosyl groups bonded to the same metal ion except a water sensitive complex $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)][PF_6]$[10], insoluble in most of the solvents. The present chapter describes syntheses, characterization and reactions of a few novel thionitrosyl complexes of ruthenium(II). Their geometries have been proposed on the basis of results from various physicochemical studies.

EXPERIMENTAL SECTION

All the reagents used were Analar or of chemically pure grade. The solvents were freshly distilled before use. Every reaction was carried out under pure, dry argon.

Trithiazyltrichloride, nitrosyl chloride, nitrosyl bromide, nitrosyl tribromide, dinitrogen trioxide, dichloro-tris(triphenylphosphine)ruthenium(II), tricarbonyl-bis(tri-phenylphosphine)ruthenium(0), carbonylchlorohydrido-tris(tri-phenylphosphine)ruthenium(II) and tribromo-tris(triphenyl-arsine)ruthenium(III) were prepared according to the methods described in the literature.[17-24]

Preparations of Complexes and Their Reactions

(i) Dichlorodithionitrosyl bis(triphenylphosphine)ruthenium(II) Dichloromethane, $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$

A solution of $(NSCl)_3$ in THF (30 ml) was added dropwise with stirring to 20 ml of a solution containing 0.8 g of

$RuCl_2(PPh_3)_3$ in chloroform at room temperature. After the addition of $(NSCl)_3$ was complete (30 min) 35 ml of dry THF was added to the solution and the stirring was further continued for about four hours. The resulting solution was almost dried under reduced pressure followed by extraction of the residue with dichloromethane. On addition of dry petroleum ether (60-80°) to CH_2Cl_2 extract, a brownish yellow complex, $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$, was precipitated which was centrifuged, washed several times with hexane and dried under vacuum (yield, 45%.). In case recrystallisation of product was carried out with the solvent, S (S = $CHCl_3$ or $CHBr_3$), the solvated product was analyzed as $[Ru(NS)_2Cl_2(PPh_3)_2].S$.

(ii) Dichloromononitrosyl-monothionitrosyl bis(triphenylphosphine)ruthenium, $[Ru(NO)(NS)Cl_2(PPh_3)_2]$

15 ml of a saturated solution of nitrosyl chloride in dichloromethane was added to 10 ml of dichloromethane solution of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ containing 0.5 g of the complex. The mixture was stirred for about 10 min. and concentrated to about 10 ml under reduced pressure. On addition of hot methanol (25 ml) to the resulting solution glistening brownish orange plates of $[Ru(NO)(NS)Cl_2(PPh_3)_2]$ were separated which were centrifuged, washed with methanol, ether and dried under vacuum. It was recrystallized from dichloromethane-methanol (1:3). Yield of the complex was increased by adding ~0.2 g triphenylphosphine to the reaction mixture.

(iii) <u>Monobromo monochloro mononitrosyl monothionitrosyl bis(tri-phenylphosphine)ruthenium, $[Ru(NO)(NS)ClBr(PPh_3)_2]$</u>

The compound was prepared by a procedure similar to that given for $[Ru(NO)(NS)Cl_2(PPh_3)_2]$ in (ii) except that 5 ml solution of nitrosyl bromide or nitrosyl tribromide (<u>ca</u>. 2 M) was used in place of nitrosyl chloride. An orange brown glistening plates of $[Ru(NO)(NS)ClBr(PPh_3)_2]$ were centrifuged, washed with methanol, ether, and dried under vacuum. It was recrystallized from dichloromethane-methanol (1:3).

(iv) <u>Dichloromonobromomonothionitrosyl bis(triphenylarsine)-ruthenium(II), $[Ru(NS)Cl_2Br(AsPh_3)_2]$</u>

A solution of $(NSCl)_3$ in THF (30 ml) was added dropwise with stirring to 30 ml of a solution containing 0.8 g of $[RuBr_3(PPh_3)_3]$ in $CHCl_3$ at room temperature. After the addition of $(NSCl)_3$, the mixture was stirred for another two hours. The resulting solution was almost dried under reduced pressure followed by the addition of petroleum ether $(60-80^0)$. The precipitate thus obtained was centrifuged, washed several times with hexane and dried under vacuum. The dried complex was further washed several times with water and dried under vacuum at 40^0C.

(v) <u>Di-μ-chloro bis[(carbonyl bis(triphenylphosphine)thioni-trosyl)]ruthenium(II) Dichloromethane, $[Ru(CO)(NS)Cl-(PPh_3)_2]_2 \cdot CH_2Cl_2$</u>

A solution of $(NSCl)_3$ in THF (20 ml) was added dropwise with stirring to 40 ml of a solution containing 0.6 g of

$[RuHCl(CO)(PPh_3)_3]$ in $CHCl_3$ at room temperature. After the addition of $(NSCl)_3$ was complete the mixture was further stirred for about two hours. The solution thus obtained was almost dried under reduced pressure and petroleum ether ($60-80°$) was added. The crude product was recrystallised three times from CH_2Cl_2-hexane (1:3).

(vi) Reaction of Trithiazyltrichloride with tricarbonyl bis(triphenylphosphine)ruthenium(0)

A solution of $(NSCl)_3$ in THF (30 ml) was added dropwise with stirring to 20 ml of a solution containing 0.5 g of $[Ru(CO)_3(PPh_3)_2]$ in THF at room temperature. After addition of $(NSCl)_3$ was complete the mixture was further stirred for one hour. The solution thus obtained was almost dried under reduced pressure and hexane was added to semidried residue. The resulting precipitate of $cis[Ru(CO)_2Cl_2(PPh_3)_2]$ was centrifuged and washed several times with hexane. $[S_4N_4]$ was recovered from the filtrate by vacuum drying.

(vii) Reaction of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ with dinitrogen trioxide

Dinitrogen trioxide gas was passed through a solution of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ (0.4 g) in CH_2Cl_2 (30 ml) for about 10 minutes. The resulting solution was concentrated under vacuum to about 10 ml followed by addition of hot methanol (ca. 30 ml). Orange crystals of $[Ru(NO)Cl_3(PPh_3)_2]$ were

separated which were centrifuged, washed with methanol, ether and dried in vacuum.

(viii) Reaction of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ with nitrosyl chloride

20 ml saturated solution of NOCl in dichloromethane was added to 15 ml of a stirred solution of $[Ru(NS)_2Cl_2(PPh_3)_2].$ CH_2Cl_2 (0.2 g) in CH_2Cl_2. The resulting mixture was refluxed for half an hour and the solution was concentrated on a water bath to about 10 ml, followed by addition of hot methanol (30 ml) whereby the orange crystals of $[Ru(NO)Cl_3(PPh_3)_2]$ were separated which were centrifuged, washed with methanol, ether and dried in vacuum.

(ix) Reaction of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ with nitrosyl bromide

10 ml solution of NOBr (ca. 2 M) in dichloromethane was added dropwise to 15 ml dichloromethane solution of $[Ru(NS)_2Cl_2-(PPh_3)_2].CH_2Cl_2$ (0.3 g). The reaction mixture was refluxed for about half an hour followed by addition of hot methanol (50 ml). Orange crystals of $[Ru(NO)Cl_2Br(PPh_3)_2]$ were separated which were centrifuged, washed with methanol, ether and dried under vacuum.

(x) Reaction of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ with nitrosyl tribromide

Orange brown glistening plates of compound $[Ru(NO)ClBr_2-(PPh_3)_2]$ were obtained by a procedure similar to that given

for $[Ru(NO)Cl_2Br(PPh_3)_2]$ in (ix) except that 10 ml solution of nitrosyl tribromide (<u>ca</u>. 2 M) was used in place of nitrosyl bromide.

(xi) Reaction of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ with X_2 ($X_2 = Cl_2$, Br_2 or I_2):

(a) <u>with chlorine</u>: Dry chlorine gas was bubbled through a solution (15 ml) of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ (0.2 g) in dichloromethane for 10 minutes and the solution was allowed to keep for an hour. On addition of hexane to it, original compound $[Ru(NS)_2Cl_2(PPh_3)_2]CH_2Cl_2.xCl_2$ was precipitated out which was washed with hexane and dried in vacuum.

(b) <u>with bromine</u>: 5 ml solution of Br_2 (0.4 ml) in CH_2Cl_2 was added to a solution of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ (0.2 g) in CH_2Cl_2 (15 ml). The original complex $[Ru(NS)_2Cl_2(PPh_3)_2]$-$CH_2Cl_2.xBr_2$ was isolated as above.

(c) <u>with iodine</u>: The dark brown coloured complex $[Ru(NS)_2Cl_2$-$(PPh_3)_2]CH_2Cl_2.xI_2$ was prepared by a procedure similar to that given in (xi(b)) except that iodine (0.2 g) in 10 ml of CH_2Cl_2 was used in place of bromine solution.

(xii) Reaction of $[Ru(NO)(NS)Cl_2(PPh_3)_2]$ with nitrosyl chloride

10 ml of a saturated solution of NOCl in CH_2Cl_2 was added to 10 ml of a stirred solution of $[Ru(NO)(NS)Cl_2(PPh_3)_2]$ (0.2 g) in dichloromethane. The reaction mixture was refluxed

for one hour, followed by addition of hot methanol (50 ml) whereby the complex, $[Ru(NO)Cl_3(PPh_3)_2]$ was separated out which was centrifuged, washed with methanol, ether and dried under vacuum.

(xiii) Reaction of $[Ru(NO)(NS)Cl_2(PPh_3)_2]$ with NOX (X = Br, or Br_3)

The orange complex $[Ru(NO)Cl_2Br(PPh_3)_2]$ was isolated by a procedure similar to that given for $[Ru(NO)Cl_3(PPh_3)_2]$ in (xii) except that 10 ml of NOBr or $NOBr_3$ solution in CH_2Cl_2 was used in place of NOCl.

(xiv) Reaction of $[Ru(NO)(NS)ClBr(PPh_3)_2]$ with NOX (X = Br, or Br_3)

Brownish orange complex $[Ru(NO)ClBr_2(PPh_3)_2]$ was isolated by a procedure similar to that given for $[Ru(NO)Cl_3(PPh_3)_2]$ and $[Ru(NO)Cl_2Br(PPh_3)_2]$ using $[Ru(NO)(NS)ClBr(PPh_3)_2]$ in place of $[Ru(NO)(NS)Cl_2(PPh_3)_2]$.

(xv) Reactions of $[Ru(NO)(NS)Cl_2(PPh_3)_2]$ with HCl and X_2 (X_2 = Cl_2, Br_2 or I_2)

To a solution of $[Ru(NO)(NS)Cl_2(PPh_3)_2]$ (0.2 g) in CH_2Cl_2 (20 ml), dichloromethane solution of X_2 (X_2 = Cl_2, Br_2 or I_2) or HCl was added. After allowing the reaction mixture to stand for about 2 hours it was refluxed for about thirty minutes. On addition of hexane (40 ml) to.it, the starting complex

$[Ru(NO)(NS)Cl_2(PPh_3)_2]$ was isolated in all the four reactions.

(xvi) Reaction of $[Ru(CO)(NS)Cl(PPh_3)_2]_2$ with nitrosyl chloride

10 ml saturated solution of NOCl in CH_2Cl_2 was added to 10 ml of a stirred solution of $[Ru(CO)(NS)Cl(PPh_3)_2]_2$ (0.2 g) in CH_2Cl_2. The reaction mixture was refluxed for 10 minutes followed by addition of hot methanol (50 ml) whereby a complex $[Ru(NO)Cl_3(PPh_3)_2]$ (yield, 40%) was separated out as a major product together with a small amount of $[Ru(CO)_2Cl_2(PPh_3)_2]$ (yield, 5%).

(xvii) Reaction of $[Ru(CO)(NS)Cl(PPh_3)_2]_2$ with NOX (X = Br or Br_3

Brownish orange complex $[Ru(NO)ClBr_2(PPh_3)_2]$ (yield, 20%) was isolated by a procedure similar to that given for $[Ru(NO)Cl_3(PPh_3)_2]$ using NOBr or $NOBr_3$ in place of NOCl together with $[Ru(CO)_2Br_2(PPh_3)_2]$ (yield, 10%).

(xviii) Reaction of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ with H_2O

$[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ (0.3 g) was stirred with 40 ml of water for 3 hr, obtained dirty green compound was centrifuged, washed several times with water, dried in air and recrystallised with dichloromethane-hexane (1:3) to get pure $[Ru(NSOH)(NS)Cl(PPh_3)_2].\frac{1}{2}CH_2Cl_2$.

Analyses and Physico-Chemical Measurements

Analyses:

Carbon, hydrogen and nitrogen analyses in the complexes were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur, India.

The percentage of sulfur in samples were determined by first heating the complex with $NaNO_3$ and NaOH (8 times and 64 times, respectively, of the amount of sample) in a nickel crucible for about 10 minutes. The cooled residue was extracted with water and acidified with HCl. It was filtered and sulfur was estimated as barium sulfate in the filtrate.

The analyses of the complexes for halogen and phosphorus were carried out by the standard methods.[25] The total chloride or bromide in the complexes was determined by fusing a weighed amount of the sample with 8 times its weight of $NaNO_3$ and 64 times its weight of NaOH in a nickel crucible for about ten minutes. After cooling it to room temperature the melt was extracted with distilled water. The insoluble impurities were filtered out and halide was estimated as silver halide in the filtrate.

For the estimation of phosphorus and arsenic, samples were decomposed by sodium peroxide, sugar and sodium nitrate in ratio 20:1:3 in a Parrbomb Crucible. The melt was extracted with water and filtered. A few ml of concentrated H_2SO_4 added to the filtrate which was slowly evaporated to sulfur trioxide

fumes. The resulting mixture was diluted with water and filtered if necessary. Phosphorus was estimated in the filtrate as phosphoammonium molybdate. For estimation of arsenic, the filtrate was diluted to 100 ml and 25 ml of the solution was taken in a 250 ml conical flask to which 40 ml water, 5 g sodium hydrogen carbonate and 2 ml of starch solution were added. The solution was swirled until the sodium hydrogen carbonate has dissolved. It was titrated slowly with the standard iodine solution to the first appearance of the blue colour.

Infrared and Raman Spectra

Infrared spectra of the compounds were recorded with a Perkin-Elmer model-580 Infrared Diffraction Grating Spectrophotometer in the 4000-200 cm^{-1} range. Samples were prepared as KBr and CsI pellets. Raman spectra were recorded on Ramalog Spex model-1443 using Spectra Physics Laser Power Source of 600 mW.

Conductivity Measurements

Conductivity of the complexes were measured on an Elico conductivity meter type CM-80 of millimolar solutions in nitrobenzene. All the compounds were found to be nonconducting.

Visible Spectra

The electronic spectra were recorded in spectroscopic grade dichloromethane and nujol mull using a Cary model-17

recording spectrophotometer.

Magnetic Susceptibility Measurements

The magnetic measurements were made using a Gouy balance. Mercurytetrathiocyanato-cobaltate(II) was used as a calibrant. All compounds were found to be diamagnetic.

Melting Points

Melting points were recorded on a Fisher-Johns melting point apparatus. The results are recorded in Table II.2.

RESULTS AND DISCUSSION

Trithiazyltrichloride reacts with dichlorotris(triphenyl-phosphine)ruthenium(II) in tetrahydrofuran giving a stable brownish yellow solid of empirical formula $[Ru(NS)_2Cl_2(PPh_3)_2]$-CH_2Cl_2.

Pyrolysis of trithiazyltrichloride at $80^{\circ}C$ has been known to result in the formation of monomeric green NSCl which exhi-bited a band due ν_{NS} at 1322 cm^{-1} in the gas phase.[26-28] Beside trithiazyltrichloride when dissolved in donor solvents such as CH_3CN, THF or DMF depolymerizes to solvated monomer NSCl to give mint green solution. The monomeric specie was also found to be present in $CHCl_3$-CCl_4. Mint green solution of trithiazyltrichloride exhibited a band due to ν_{NS} at 1010 cm^{-1}, the position of which is comparable to the one

(1008 cm^{-1}) observed in the i.r. spectrum of the solid compound in nujol mull. Possibly the collisions between trithiazyltrichloride and complex molecules generates enough activation energy to depolymerize trithiazyltrichloride to monomeric species.

Above dithionitrosyl complex on recrystallization from solvent/hexane (solvent = CH_2Cl_2, $CHCl_3$ or $CHBr_3$) gave stable, diamagnetic and nonconducting solvated complexes whose analytical data correspond to $[Ru(NS)_2Cl_2(PPh_3)_2]$.solvent (Table II.1). They were soluble in dichloromethane, chloroform, and insoluble in hexane and petroleum ether. The i.r. spectra of these complexes (Fig. II.I(1)) showed absorption bands at 1300 cm^{-1}, 1120 cm^{-1} and 330 cm^{-1} besides the characteristic bands of triphenylphosphine.[29] The band at 330 cm^{-1} was assigned to terminal Ru-Cl stretching mode and ones, at 1300 cm^{-1} and 1120 cm^{-1} to the coordinated NS$^+$ [7-11] and NS$^-$ [15,16] groups respectively. Alternatively, the band at 1120 cm^{-1} could be due to $\nu_{P=0}$ of the coordinated triphenylphosphine oxide formed as a result of oxidation of PPh_3 by NSCl. But this possibility is ruled out by the facts: (1) that $OPPh_3$ was not recovered from the filtrates of any of the reactions after removal of the complex, (2) that the reactions were carried out in oxygen-free argon atmosphere and the possibility of the extraction of oxygen by PPh_3 from the solvent to form $OPPh_3$ is remote and (3) that the percentages of sulfur and nitrogen in the complex corresponds to the presence of two NS groups. It will, further

be interesting to note that the difference in the two frequencies between the two $\nu_{(NS)}$ bands is of the same order as that observed for $[Ru(NO)_2Cl(PPh_3)_2][PF_6]$ (ν_{NO}, 1845 cm^{-1} and 1687 cm^{-1}).[30] It has, therefore, been presumed that the complex contains thionitrosyl groups bonded to ruthenium one as NS$^+$ and another as NS$^-$. However, the coupling between two NS groups, in the cis position to give bands due to $\nu_{asy(NS)}$ and $\nu_{sym(NS)}$ exists, but the first formulation is preferred over the second one because of the differences in the reactivities of two NS groups towards various reagents e.g., NOX, N_2O_3, $NOBr_3$ or water.

Raman spectrum of $[Ru(NS)_2Cl_2(PPh_3)_2]$ (Fig. II.III) showed bands at 1121 and 1300 cm^{-1} and that of $[Ru(NO)(NS)Cl_2$-$(PPh_3)_2]$ at 1310 cm^{-1} besides the characteristic bands of triphenylphosphine. The positions of bands in Raman spectra matched with those observed in infrared spectra.

The presence of CH_2Cl_2 as solvated molecule is also indicated by its replacement by other halogenated molecules like $CHCl_3$ and $CHBr_3$ when $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ was recrystallised in $CHCl_3$ or $CHBr_3$ medium. The solvent molecule may also be introduced in the complex if the synthetic reactions were carried out in CH_2Cl_2 or $CHBr_3$ in place of $CHCl_3$.

The reaction of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ with H_2O yielded a diamagnetic dirty green complex whose IR spectrum (Fig. II.I(4)) showed the absence of the band at 1300 cm^{-1}

and appearance of new bands at 3200 cm^{-1}(br), 1630 cm^{-1}, 1280 cm^{-1} and 1030 cm^{-1} which can be attributed to coordinated NSOH group.[31-33] The results of analysis indicated its formulation as $[Ru(NSOH)(NS)Cl(PPh_3)_2].\frac{1}{2}CH_2Cl_2$ in which ruthenium should be in +2 oxidation state as also evidenced by its diamagnetic behaviour. This suggested the nucleophilic attack of OH^- ion on the NS^+ moiety of the complex with the formation of NSOH.

Reactions of $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ with NOX (X = Cl, Br or Br_3) gave diamagnetic, nonconducting nitrosyl-thionitrosyl complexes $[Ru(NO)(NS)ClX(PPh_3)_2]$ (X = Cl or Br) whose IR spectrum (Fig. II.I(2)) showed the replacement of a band at 1120 cm^{-1} assigned to ν_{NS}^- by a new band at 1880 cm^{-1} characteristic of ν_{NO}^+ while the position of other band due to ν_{NS}^+ remained practically constant (1320 cm^{-1}). In case the coupling between the two modes of NS stretching existed, the position of ν_{NS} at 1300 cm^{-1} should also be changed or lowered slightly. The shifting of the thionitrosyl stretching frequency towards higher energy (ν_{NS}, 1320 cm^{-1}) than that displayed by the dithionitrosyl complex (ν_{NS}, 1300 cm^{-1}) may be due to decrease in electron density at the metal centre which manifests itself in less back donation from the metal to NS π^* orbitals.

The replacement of NS^- by NO^+ has also been reported by the reactions of NOX (X = Cl, Br or Br_3) with $[Rh(CO)(NS)Cl_2-(PPh_3)_2]$ in which NS is coordinated as NS^- to form

$[Rh(CO)(NO)ClX(PPh_3)_2]$ (X = Cl or Br) where NO is coordinated as NO^+.[15] Further the reactions of $[NSCl]$ with series of nitrosyl complexes having coordinated NO^+ or NO^- indicated the replacement of NO^- by NS.[34] Possibly in these reactions there is an electrophilic attack of NO^+ on NS^- which is contrary to the one by OH^- where the nature of attack is nucleophilic.

The nitrosyl-thionitrosyl complexes $[Ru(NO)(NS)ClX(PPh_3)_2]$ (X = Cl or Br) are nonelectrolyte, diamagnetic crystalline solids. These complexes are so stable that no reaction was observed with chlorine, bromine and iodine. But on refluxing dithio or mononitrosyl monothionitrosyl dihalide complexes with excess of NOCl, NOBr, $NOBr_3$ and N_2O_3, ruthenium nitrosyl complexes of the type $[Ru(NO)ClX_2(PPh_3)_2]$ (X = Cl or Br) have been obtained. The nitrosyl stretching frequencies in $[Ru(NO)ClX_2(PPh_3)_2]$ (X = Cl or Br) were found to be in the range observed for nitrosyl complexes of ruthenium(II).[35]

$[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$ + NOX

Room Temp.
CH_2Cl_2

NOX
Reflux

$[Ru(NO)(NS)ClX(PPh_3)_2]$

NOX
Reflux

$[Ru(NO)ClX_2(PPh_3)_2]$
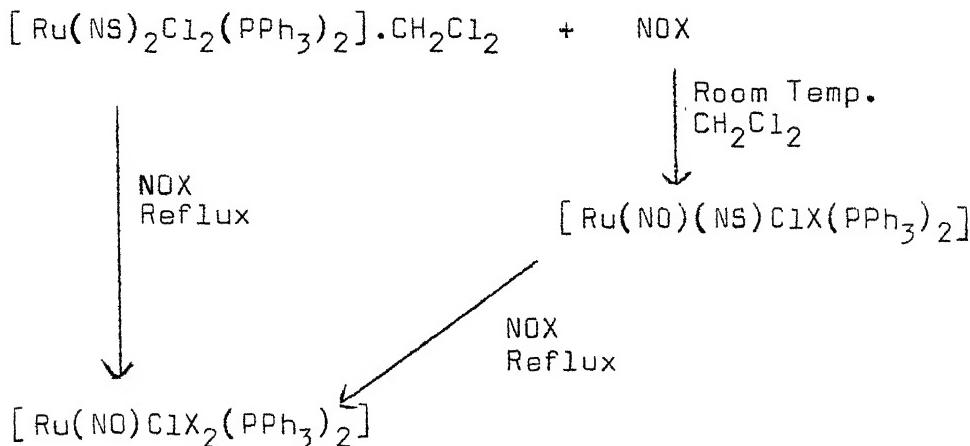
Dithionitrosyl $[Ru(NS)_2Cl_2(PPh_3)_2]$ formed solvent adducts with chloroform, dichloromethane and bromoform. The adducts on treatment with iodine, bromine and chlorine possibly gave charge transfer $(CH_2Cl_2-I, Br$ or $Cl)$ complexes as indicated by the fact that the $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2.xX_2(X = I, Br$ or $Cl)$ showed electronic absorption bands in the same region (Fig. II.II) of visible spectra as the positions of bands in the spectra of the dichloromethane solutions of iodine, bromine and chlorine.

IR spectrum of the complex $[Ru(NS)Cl_2Br(AsPh_3)_2]$ showed (Fig. II.I(6)) absorption bands at 1295 cm^{-1} and 330 cm^{-1} besides the characteristic bands of triphenylarsine. The band at 330 cm^{-1} was assigned to terminal Ru-Cl stretching mode and the one at 1295 cm^{-1} to the coordinated NS^+. IR spectrum of the complex $[Ru(CO)(NS)Cl(PPh_3)_2]_2$ (Fig.II.I(5)) showed absorption bands at 2075 cm^{-1}, 1960 cm^{-1}(br), 1115 cm^{-1} and 280 cm^{-1}. The band at 280 cm^{-1} was assigned to bridging Cl, 1115 cm^{-1} to $\nu_{NS}-$ and ones at 2075 cm^{-1} and 1960 cm^{-1} to the ν_{CO}. $[Ru(CO)(NS)Cl(PPh_3)_2]_2$ on treatment with NOCl, NOBr and $NOBr_3$ gave monomeric species $[Ru(NO)ClX_2(PPh_3)_2]$ (X = Cl or Br) as a major product and small amounts of $[Ru(CO)_2X_2(PPh_3)_2]$ were also obtained. It will be interesting to note that the percentage yield of nitrosyl complexes vary with the stability of NOX in $CH_2Cl_2(NOCl > NOBr > NOBr_3)$ while that of dicarbonyl complexes in the reverse order. It could possibly be related to the time for which NO remains in solution.

Reaction of $[Ru(CO)_3(PPh_3)_2]$ with $(NSCl)_3$ gave cis-dicarbonyl complex $[Ru(CO)_2Cl_2(PPh_3)_2]$ having characteristic ν_{CO} frequencies (Fig. II.I(7)) at 2064 cm^{-1} and 2001 cm^{-1}.[36] Tetrasulfur tetranitride (Fig. II.I(8)) was also recovered from this reaction mixture. The reduction of trithiazyltrichloride to tetrasulfur tetranitride by iron and copper[37] has been reported recently, but only one report[38] is available in which complex has been used for the reduction of $(NSCl)_3$. This novel and simple route for the preparation of S_4N_4 is of importance since it is one of the most valuable starting material for preparing other inorganic sulfur nitrogen compounds.

Table II.1. Analytical data of the complexes

Compound	ANALYSES Calculated (Found) %					
	C	H	N	S	Cl/Br	P/As
1	2	3	4	5	6	7
[Ru(NS)$_2$Cl$_2$(PPh$_3$)$_2$].CH$_2$Cl$_2$	50.8 (50.5)	3.6 (3.6)	3.2 (3.3)	7.3 (7.2)	16.2 (16.4)	7.1 (7.0)
[Ru(NS)$_2$Cl$_2$(PPh$_3$)$_2$].CHCl$_3$	48.9 (48.8)	3.4 (3.5)	3.1 (3.2)	7.0 (6.9)	19.5 (19.6)	6.8 (6.9)
[Ru(NS)$_2$Cl$_2$(PPh$_3$)$_2$].CHBr$_3$	42.6 (42.3)	3.0 (3.2)	2.7 (2.8)	6.1 (6.2)	29.8 (30.0)	5.9 (5.8)
[Ru(NO)(NS)Cl$_2$(PPh$_3$)$_2$]	55.9 (55.8)	3.9 (3.8)	3.6 (3.5)	4.1 (4.0)	9.2 (10.0)	8.0 (8.1)
[Ru(NO)(NS)BrCl(PPh$_3$)$_2$]	52.9 (53.0)	3.7 (3.5)	3.4 (3.4)	3.9 (3.8)	14.1 (14.6)	7.6 (7.7)
[Ru(NS)Cl$_2$Br(AsPh$_3$)$_2$]	47.5 (47.8)	3.3 (3.1)	1.5 (1.6)	3.5 (3.4)	16.6 (16.8)	16.4 (16.1)
[Ru(CO)(NS)Cl(PPh$_3$)$_2$]$_2$.CH$_2$Cl$_2$	57.9 (56.8)	4.0 (3.9)	1.8 (1.9)	4.1 (4.3)	9.1 (8.9)	8.0 (8.1)
[Ru(NO)Cl$_3$(PPh$_3$)$_2$]	56.7. (56.9)	3.9 (3.8)	1.8 (1.9)	-- --	14.0 (14.2)	8.1 (8.0)

Table II.1 (contd.)

	1	2	3	4	5	6	7
$[Ru(NO)Cl_2Br(PPh_3)_2]$		53.6 (53.4)	3.7 (3.7)	1.7 (1.9)	-- --	18.7 (18.8)	7.7 (7.6)
$[Ru(NO)ClBr_2(PPh_3)_2]$		50.8 (50.9)	3.5 (3.4)	1.6 (1.7)	-- --	22.9 (23.0)	7.3 (7.4)
$[Ru(NSOH)(NS)Cl(PPh_3)_2].\frac{1}{2}CH_2Cl_2$		53.9 (52.0)	3.8 (3.9)	3.4 (3.8)	7.9 (8.1)	8.7 (8.9)	7.6 (7.4)

Table II.2. Colour, melting point and important infrared frequencies of the complexes

			Infrared Frequencies			
Compound	Colour	M.P. (°C)	ν_{NS} (cm⁻¹)	ν_{NO} (cm⁻¹)	ν_{CO} (cm⁻¹)	Other freq. (cm⁻¹)
1	2	3	4	5	6	7
$[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$	Brownish yellow	128	1300, 1120	-	-	330
$[Ru(NS)_2Cl_2(PPh_3)_2].CHCl_3$	Brownish yellow	126	1300, 1120	-	-	329
$[Ru(NS)_2Cl_2(PPh_3)_2].CHBr_3$	Brown	123	1300, 1120	-	-	329
$[Ru(NO)(NS)Cl_2(PPh_3)_2]$	Brownish orange	198	1320	1880	-	330
$[Ru(NO)(NS)ClBr(PPh_3)_2]$	Orange brown	188	1320	1878	-	330
$[Ru(NS)Cl_2Br(AsPh_3)_2]$	Brown	>250	1295	-	-	329
$[Ru(CO)(NS)Cl(PPh_3)_2]_2.CH_2Cl_2$	Brown	149	1115	-	2075 1960(br)	280
$[Ru(NO)Cl_3(PPh_3)_2]$	Orange	242	-	1878	-	330

Table II.2 (contd.)

1	2	3	4	5	6	7
$[Ru(NO)Cl_2Br(PPh_3)_2]$	Orange	238	-	1877	-	329
$[Ru(NO)ClBr_2(PPh_3)_2]$	Brownish orange	235	-	1875	-	330
$[Ru(NSOH)(NS)Cl(PPh_3)_2].\frac{1}{2}CH_2Cl_2$	Dirty green	>250	1120	-	-	3200(br), 1630, 1280, 1030, 330

LEGEND TO THE FIGURES

Fig. II.I. Infrared Spectra of the Complexes in KBr discs:

(1) $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$

(2) $[Ru(NO)(NS)Cl_2(PPh_3)_2]$

(3) $[Ru(NO)Cl_3(PPh_3)_2]$

(4) $[Ru(NSOH)(NS)Cl(PPh_3)_2].\frac{1}{2}CH_2Cl_2$

(5) $[Ru(CO)(NS)Cl(PPh_3)_2]_2.CH_2Cl_2$

(6) $[Ru(NS)Cl_2Br(AsPh_3)_2]$

(7) $[Ru(CO)_2Cl_2(PPh_3)_2]$

(8) $[S_4N_4]$

Fig. II.II. Electronic Spectra

(1) I_2 in CH_2Cl_2

(2) Br_2 in CH_2Cl_2

(3) Cl_2 in CH_2Cl_2

(4) $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2.xI_2^*$

(5) $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2.xBr_2^*$

(6) $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2.xCl_2^*$

$* = $ Nujol mull

Fig.II.III. Raman Spectra of Solid Samples

(1) $[Ru(NS)_2Cl_2(PPh_3)_2].CH_2Cl_2$

(2) $[Ru(NO)(NS)Cl_2(PPh_3)_2]$

INFRARED SPECTRA

Fig. II. I

WAVENUMBER CM^{-1}x10^{-2}

INFRARED SPECTRUM

Fig. II.I

% Transmittance (arb. scale)

(4)

% Transmittance (arb. scale)

Frequency cm^{-1} x 10^{-2}

INFRARED SPECTRA

Fig. II.I

(5)

(6)

INFRARED SPECTRA

Fig. II. I

ELECTRONIC SPECTRA

Fig. II.II

(1)

(2)

Absorbance (arb. scale)

700   800   900   1000   1100   1200   1300   14

Frequency cm⁻¹

RAMAN SPECTRA
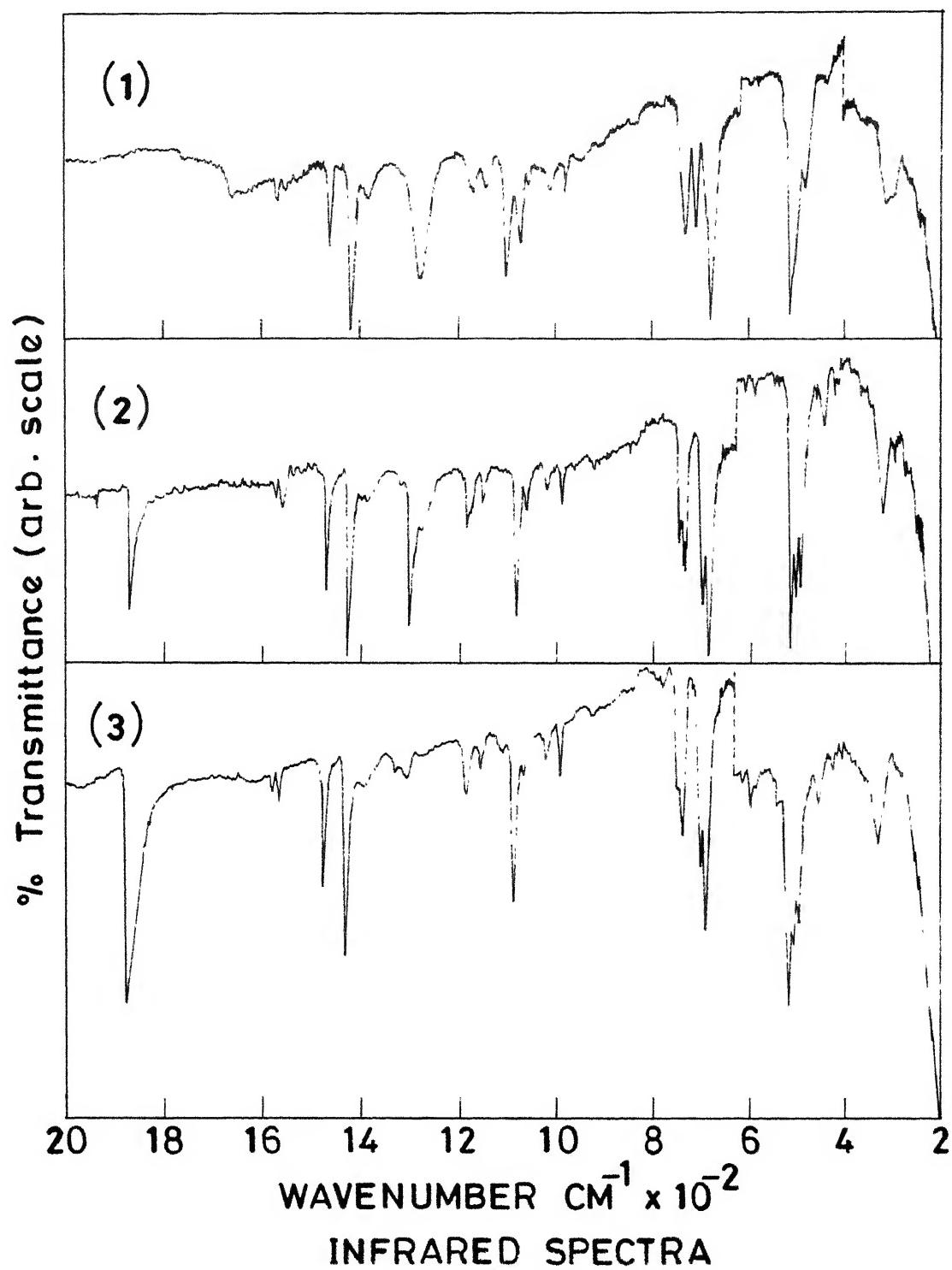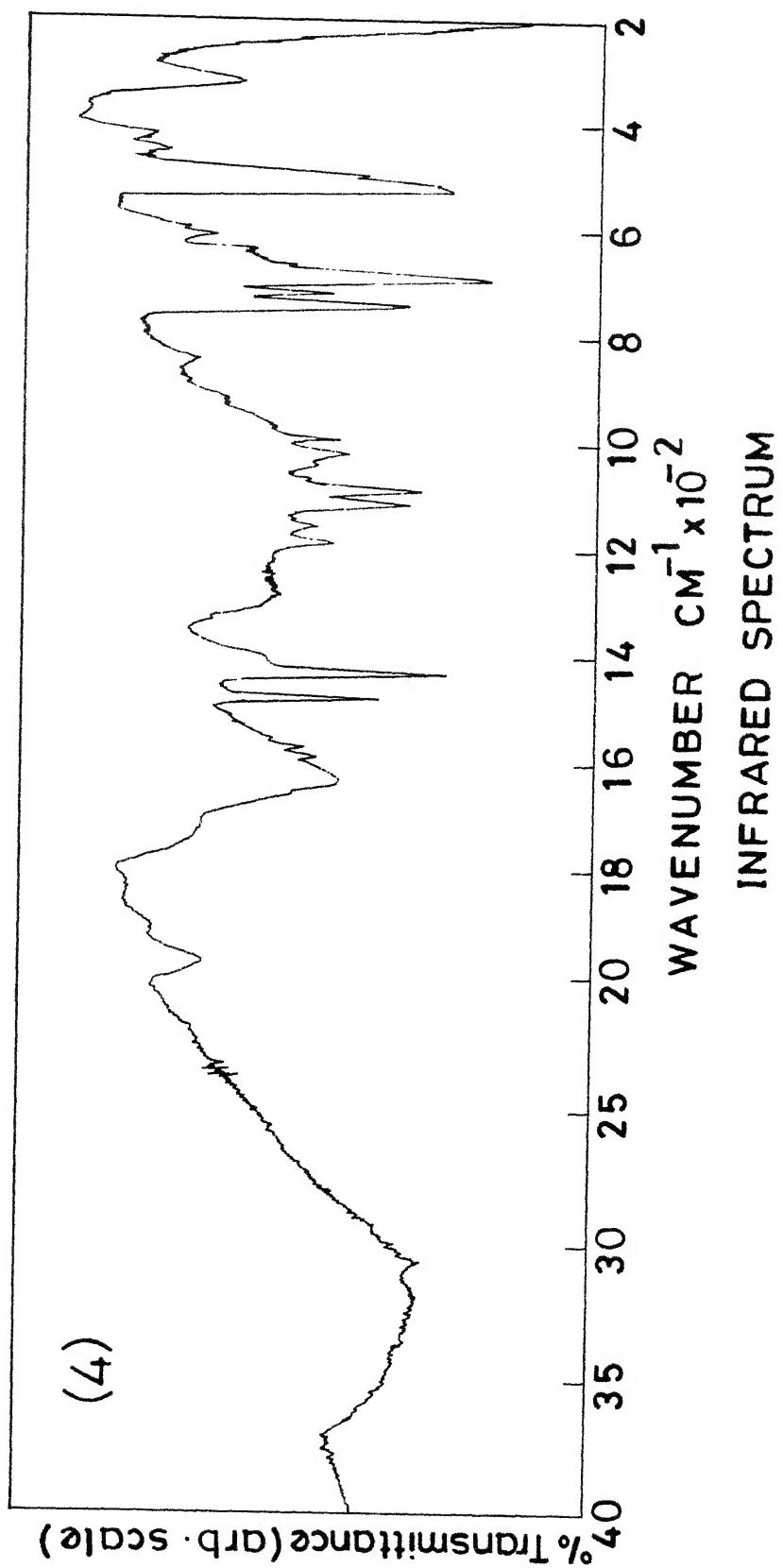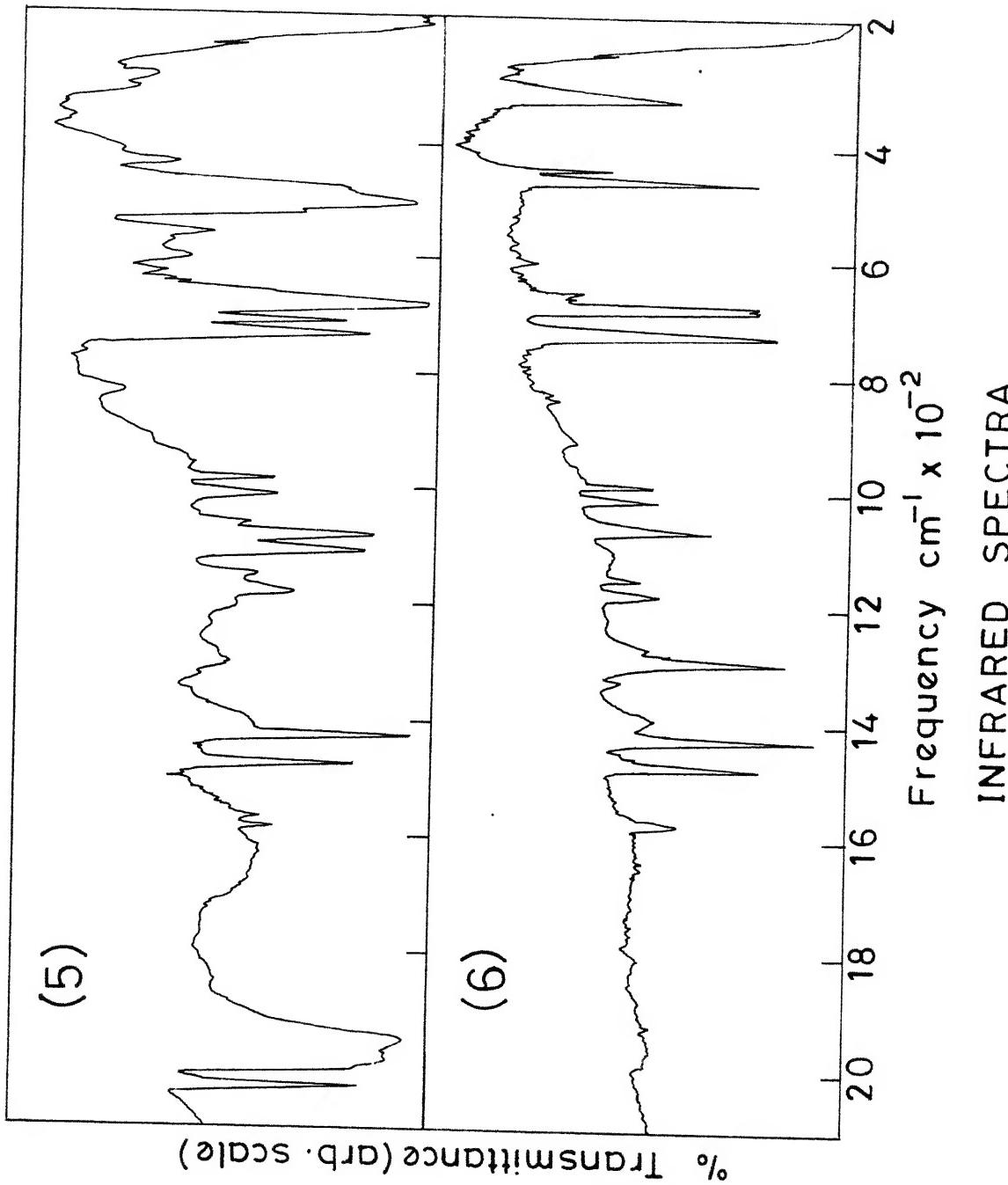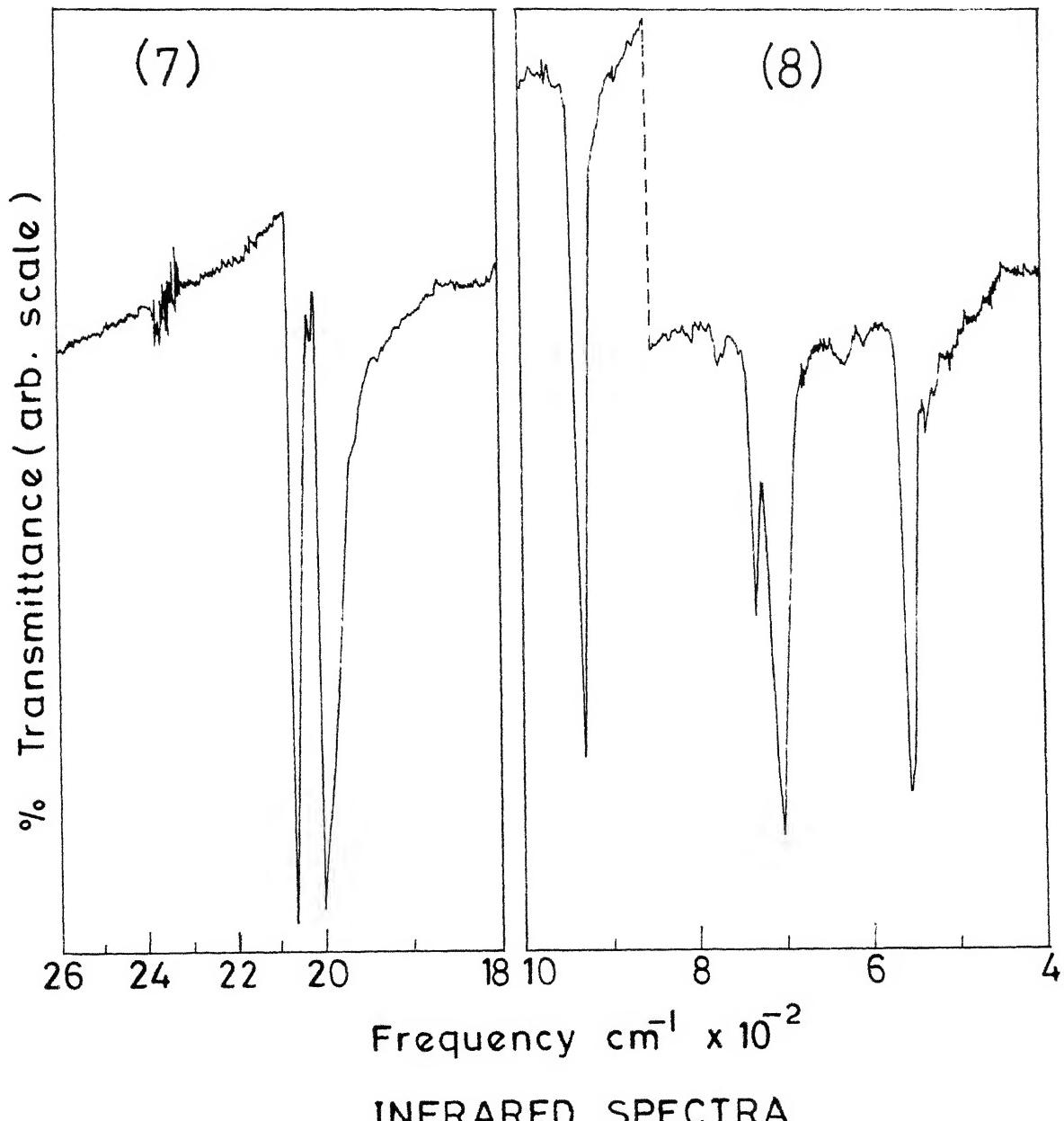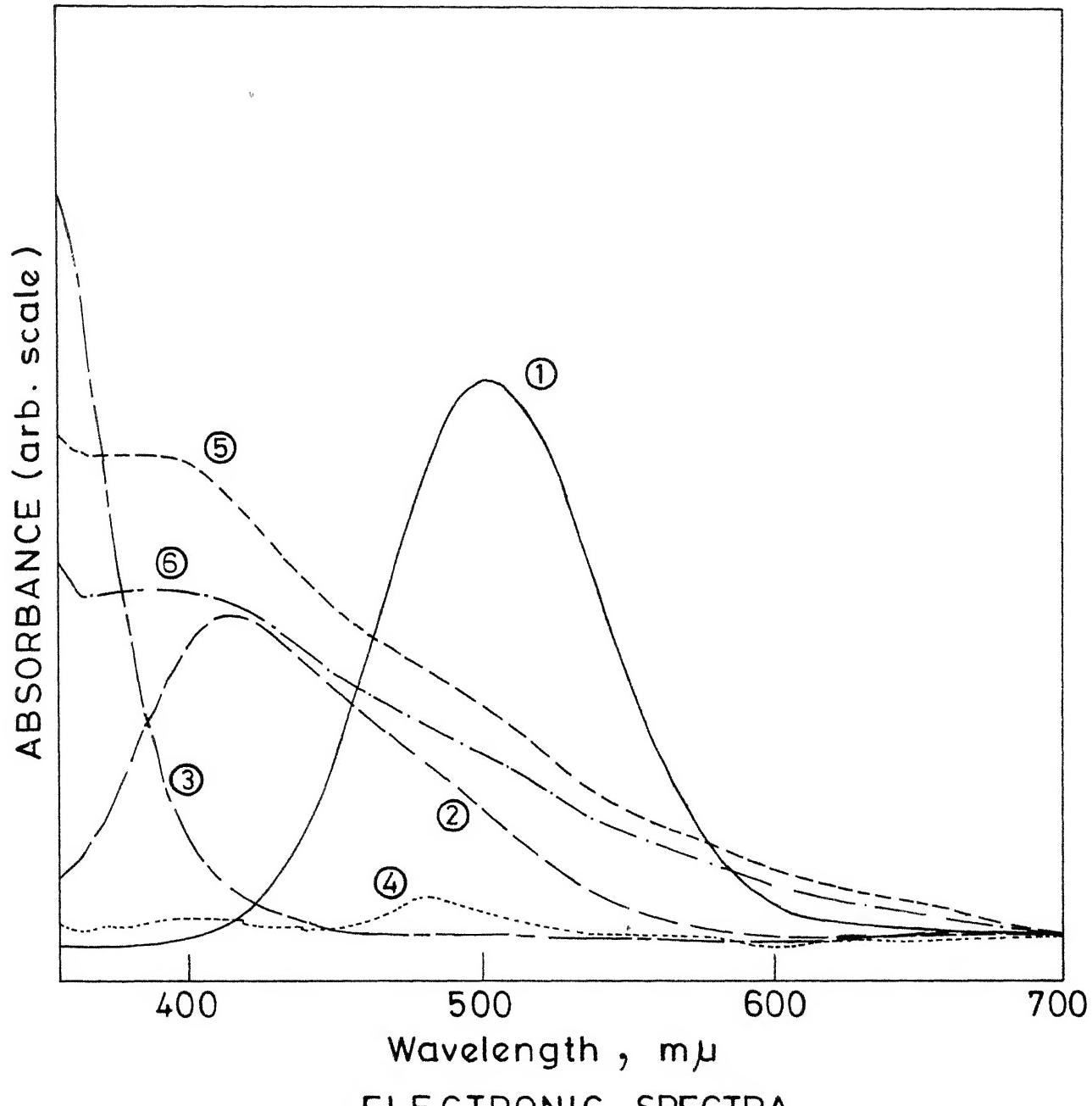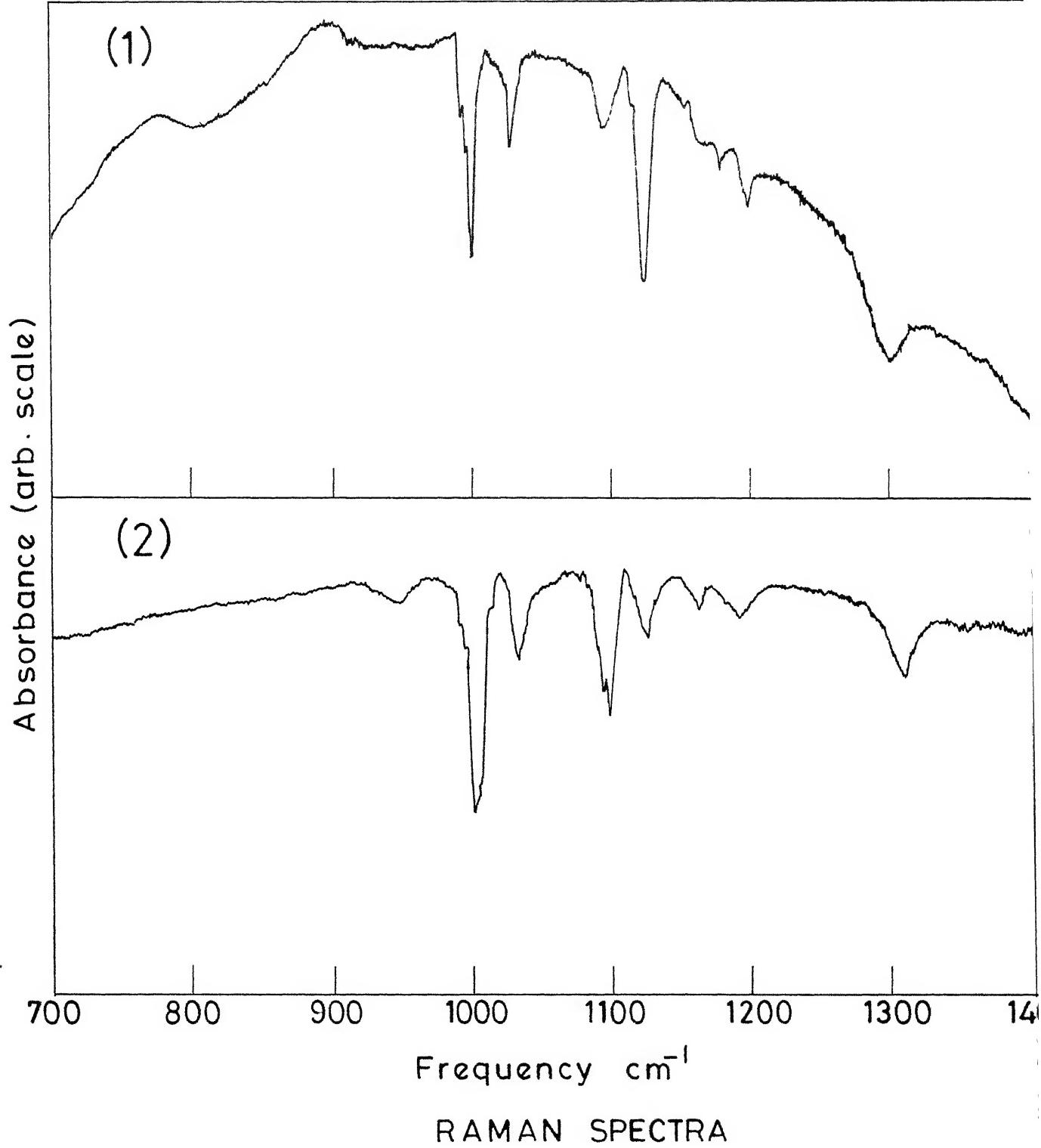
Fig . II .III

REFERENCES

1. B.F.G. Johnson and J.A. McCleverty, Prog. Inorg. Chem., 7, 277 (1966).

2. W.P. Griffith, Adv. Organomet. Chem., 7, 211 (1968).

3. N.G. Connelly, Inorg. Chim. Acta Rev., 6, 46 (1972).

4. K.G. Caulton, Coord. Chem. Rev., 14, 317 (1974).

5. F. Bottomley, Coord. Chem. Rev., 26, 7 (1978).

6. J.A. McCleverty, Chem. Rev., 79, 53 (1979).

7. J. Chatt and J.R. Dilworth, J. Chem. Soc. Chem. Comm., 508 (1974).

8. M.W. Bishop, J. Chatt and J.R. Dilworth, J. Chem. Soc. Chem. Comm., 780 (1975).

9. M.W. Bishop, J. Chatt and J.R. Dilworth, J. Chem. Soc. Dalton Trans., 1 (1979).

10. B.W.S. Kolthammer and P. Legzdins, J. Am. Chem. Soc., 100, 2247 (1978).

11. K.K. Pandey and U.C. Agarwala, Z. Anorg. Allgem. Chem., 461(2), 231 (1980).

12. T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, J. Chem. Soc. Chem. Comm., 1036 (1978).

13. T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, Inorg. Chem., 18, 3548 (1979).

14. M.B. Hursthouse and M. Motevalli, J. Chem. Soc. Dalton Trans., 1362 (1979).

15. K.K. Pandey, K.C. Jain and U.C. Agarwala, Inorg. Chim. Acta, 48, 23 (1981).

16. K.C. Jain, K.K. Pandey, S.S. Katiyar and U.C. Agarwala, Int. Conf. Coord. Chem.,1980, p. 440.

17. W.L. Jolly and K.D. Maguire, Inorg. Synths., 9, 102 (1967).

18. Shell Internat. Research Maatschappij, N.U. Neth. Appl., 61512661 (CI.C015), 31, 3 (1967).

19. W.G. Burn and H.J. Bernsterin, J. Chem. Phys., 18, 1669 (1950).

20. R.L. Datta and N.R. Chatterjee, J. Am. Chem. Soc., 45, 481 (1923).

21. G. Brauer, Handbook of Preparative Inorganic Chemistry (Academic Press, New York), 1, 488 (1963).

22. P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., 12, 237 (1970).

23. N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley Inorg. Synth., 15, 50 (1974).

24. K. Natarajan, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India (1976).

25. A.I. Vogel, A textbook of Quantitative Inorganic Analysis, 3rd Edn., Longmans Green, London (1961).

26. R.L. Patton and W.L. Jolly, Inorg. Chem., 9, 1079 (1970).

27. N.R.D. Barton and A.W. Bubb, J. Chem. Soc., Perkin Trans., 916 (1977).

28. A. Muller, N. Mohan, O. Glemser, S.J. Cyvin and N. Weinstock, J. Mol. Spectrosc., 59, 161 (1976).

29. J.C. Sheldon and S.Y. Tyree Jr., J. Am. Chem. Soc., 80, 2120 (1958).

30. C.G. Pierpont and R. Eisenberg, Inorg. Chem., 11, 1088 (1972).

31. P.O. Tchir and R.D. Spratley, Can. J. Chem., 53, 2318 (1975).

32. V.R. Mews and H.C. Brauer, Z. Anorg. Allgem. Chem., _447_, 126 (1978).

33. A.A. Bhattacharya, A.G. Turner, Inorg. Chim. Acta, _44_, L185 (1980).

34. K.K. Pandey and U.C. Agarwala, Inorg. Chem., _20_(4), 1308 (1981).

35. K.C. Jain, K.K. Pandey, R. Parashad, T. Singh and U.C. Agarwala, Ind. J. Chem., _19A_, 1089 (1980).

36. B.R. James and L.D. Markham, Inorg. Nucl. Chem. Lett., _7_, 373 (1971).

37. M.P. Berthen, H. Vinneht and Y. Monteil, Z. Naturforsch., _B35_, 329 (1980).

38. R.D. Tiwari, K.K. Pandey and U.C. Agarwala, Inorg. Chem. (in press).

CHAPTER III

THIONITROSYL COMPLEXES OF RHODIUM, IRIDIUM AND THIAZATE COMPLEXES OF RHODIUM

During the last few years, some work has been published relating to synthetic and structural aspects of metal thio-nitrosyl complexes[1-11] in which thionitrosyl group has been shown to be terminally bonded.[8-10] There is, however, only one report of each where (1) a bridge through thionitrosyl group between two rhodium atoms[12] has been postulated and (2) thiazate group coordinated to iridium.[13] Although NSO group has been known in the form of organic sulphinylamines for more than a century,[14] covalent derivatives of the other elements have been synthesized recently.[15-20] Other permutations of the atoms of this group are known. HOSN is only briefly stable at room temperature, readily polymerises and forms red violet deriva-tives LiOSN and NaOSN.[21] This chapter describes the syntheses and the characterisation of thionitrosyl complexes of rhodium and iridium having terminal or bridged thionitrosyl group together with thiazate complexes of rhodium. Their tentative

geometries have been proposed on the basis of the results of various physico-chemical studies.

EXPERIMENTAL SECTION

All reagents used were analar or of chemically pure grade. The solvents were dried and freshly distilled before use. All the reactions were carried out under pure and dry argon atmosphere.

Chlorotris(triphenylphosphine)rhodium(I), dichloronitrosylbis(triphenylphosphine)rhodium(III), dibromonitrosylbis-(triphenylphosphine)rhodium(III), hydridotetrakis(triphenyl-phosphine)rhodium(I), carbonylchlorobis(triphenylphosphine)-rhodium(I), trithiazyltrichloride and NSOH were prepared by the literature methods.[21-26]

(i) Reaction of $[Rh(NO)Cl_2(PPh_3)_2]$ with $(NSCl)_3$ at room-temperature

30 ml of a green solution (ca. 3 mmol) of $(NSCl)_3$ in THF was added dropwise to a stirring solution of $[Rh(NO)Cl_2(PPh_3)_2]$ (0.4 g) in dry chloroform (30 ml) at room temperature. The resulting solution was further stirred for about 2 hours and the solvent was completely removed under reduced pressure. The residue was extracted with benzene. On addition of petroleum ether (60-80°) to the extract, di-μ-chlorobis(chloro-thionitrosyltriphenylphosphine)rhodium(III), $[Rh(NS)Cl_2(PPh_3)]_2$

was   precipitated out which was filtered and washed several times with hexane and water. It was dried in air and recrystallized from benzene-hexane.

(ii) Reaction of di-μ-chlorobis(chlorothionitrosyltriphenyl-phosphine)rhodium(III), [Rh(NS)Cl$_2$(PPh$_3$)]$_2$, with triphenyl-phosphine

Triphenylphosphine (0.4 g) was dissolved in 20 ml solution of [Rh(NS)Cl$_2$(PPh$_3$)]$_2$ (0.2 g) in dichloromethane. The resulting solution was refluxed for 1 hour. On addition of hexane to it, a red brown complex [Rh(NS)Cl$_2$(PPh$_3$)$_2$] was precipitated out which was centrifuged, washed with ether and dried in vacuum. It was recrystallised from benzene-hexane (3:1).

(iii) Reaction of [Rh(NO)Br$_2$(PPh$_3$)$_2$] with (NSCl)$_3$

30 ml of a green solution of (NSCl)$_3$ (ca. 3 mmol) in THF was added dropwise to a stirred solution of [Rh(NO)Br$_2$-(PPh$_3$)$_2$] (0.2 g) in CHCl$_3$ (30 ml) at 10^{0}C. The resulting solution was stirred for 2 hours and solvent was evaporated under reduced pressure. The residue was extracted with benzene. On adding hexane to the extract, a brown complex di-μ-thio-nitrosylbis(dichlorotriphenylphosphine)rhodium(III) was precipitated out which was centrifuged, washed with hexane, water and dried in air. It was recrystallized as brown crystals, [Rh(NS)Cl$_2$(PPh$_3$)]$_2$ from toluene-dichloromethane (1:1).

(iv) Reaction of [RhH(PPh₃)₄] with (NSCl)₃

30 ml of a green solution of (NSCl)₃ (ca. 3 mmol) was added dropwise with stirring to a solution of [RhH(PPh₃)₄] (0.2 g) in THF (30 ml) at 10°C. The resulting solution was stirred for two hours at 10°C. Brown crystals of [Rh(NS)Cl₂-(PPh₃)]₂ were isolated by the procedure similar to that given in (iii).

(v) Reaction of IrCl₃.xH₂O with triphenylphosphine in presence of NO gas

IrCl₃.xH₂O (0.4 g) and methanol (20 ml) were heated under reflux for ca. 1½ hr. A stream of nitric oxide was bubbled through the solution. Triphenylphosphine (1.05 g) and methanol (10 ml) were added to the solution and the mixture was heated under reflux for about 1 hr. Yellow crystals of [IrHCl₂(PPh₃)₃] were separated on cooling, centrifuged, washed with a little water (∼2 ml), methanol (∼2 ml) and ether (∼2 ml) and dried under vacuum.

(vi) Reaction of (NSCl)₃ with [IrHCl₂(PPh₃)₃]

A green solution of (NSCl)₃ in THF (20 ml) was added dropwise to a stirred solution of [IrHCl₂(PPh₃)₃] (0.3 g) in THF (20 ml) at 10°C. The resulting solution was stirred for about one hour. Solvent was evaporated under reduced pressure and the residue thus obtained was extracted with benzene. On adding hexane to the extract, a yellowish brown compound was

precipitated out which was centrifuged, washed with hexane
and dried in vacuum. It was recrystallized as $[Ir(NS)Cl_2-$
$(PPh_3)_2]$ from benzene-dichloromethane (1:1).

(vii) Reaction of small amount of NSOH with $[Rh(CO)Cl(PPh_3)_2]$

A solution of NSOH in $CHCl_3$ (10 ml) was added dropwise
to a stirred chloroform solution of $[Rh(CO)Cl(PPh_3)_2]$ (0.2 g)
at $20^{\circ}C$. The resulting mixture was stirred for about twenty
minutes. Solvent was evaporated under reduced pressure and the
residue was extracted with benzene. A yellowish green compound,
$[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$ was precipitated out on addition
of hexane to the extract. It was centrifuged, washed with
pentane, water and dried in air.

(viii) Reaction of excess of NSOH with $[Rh(CO)Cl(PPh_3)_2]$

A solution of NSOH in $CHCl_3$ (25 ml) was added dropwise
to a stirred chloroform solution of $[Rh(CO)Cl(PPh_3)_2]$ (0.2 g)
and the reaction mixture was stirred for an hour. A brown
complex, $[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$ was obtained by the procedure
similar to that described for $[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$ in (vii).

(ix) Reaction of NSOH with $[RhCl(PPh_3)_3]$

A solution of NSOH in chloroform (25 ml) was added drop-
wise to a stirred chloroform solution of $[RhCl(PPh_3)_3]$ (0.2 g)
at room temperature. The resulting solution was further

stirred for about one hour. A brown complex,$[Rh(H_2O)(NSO)_2Cl-(PPh_3)]_2$ was obtained by the procedure similar to that described for $[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$ in (vii).

(x) Reaction of triphenylphosphine with $[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$

Triphenylphosphine (0.3 g) was dissolved in 20 ml solution of $[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$ (0.2 g) in chloroform. The resulting solution was refluxed for 1 hour. On addition of hexane, a light brown complex $[Rh(H_2O)(NSO)_2Cl(PPh_3)_2]$ was precipitated out which was centrifuged, washed with ether and dried in vacuum. It was recrystallized twice from benzene-hexane (1:3).

The analyses of carbon, hydrogen, nitrogen, phosphorus, melting points, infrared spectra, conductivity and magnetic susceptibilities of the complexes were obtained by the methods given in Chapter II. The rhodium, chloride and sulfur analyses were carried out by the standard methods.[27,28] The results are given in Table III.1 and Table III.2. Molecular weights were determined cryoscopically in dry benzene.

RESULTS AND DISCUSSION

Reaction of $(NSCl)_3$ in THF with $[Rh(NO)Br_2(PPh_3)_2]$ at low temperature gave a brown complex $[Rh(NS)Cl_2(PPh_3)]_2$

$SPPh_3$ and $OPPh_3$ were recovered from the washings and analysed.

A plausible mechanism could involve the prior formation of a six coordinated intermediate sulfurmonoxide[12] complex, $[Rh(NS)(SO)Cl_2(PPh_3)]_2$ which reacted readily with triphenylphosphine to give $[Rh(NS)Cl_2(PPh_3)]_2$, $SPPh_3$ and $OPPh_3$. The formation of triphenylphosphine sulfide and triphenylphosphine-oxide in the reaction of sulfurmonoxide complex $[Ir(SO)_2(dppe)_2]-Cl$ with triphenylphosphine have been reported by Schmid and Ritter.[29,30] Bromogroups present in the starting complex were substituted by the chlorides, possibly from $(NSCl)_3$. The same bridged thionitrosyl complex $[Rh(NS)Cl_2(PPh_3)]_2$ could also be formed by the interaction of $[Rh(NO)Cl_2(PPh_3)_2]$ with $(NSCl)_3$ as reported previously.[12]

The complex $[Rh(NS)Cl_2(PPh_3)]_2$ is air stable nonelectrolyte in nitrobenzene, diamagnetic, soluble in THF, benzene, dichloromethane and insoluble in hexane and ether. The molecular weight was found to be 900, suggesting its dimeric nature. The absence of the band at 1630 cm^{-1} due to ν_{NO} present in the starting complex and the appearance of a new band at 840 cm^{-1} assigned to bridged ν_{NS} in the spectrum of the complex (Fig. III.I(1)) suggested the substitution of nitrosyl by thionitrosyl group. One might expect two bands due to ν_{NS} because of the coupling of two NS groups in the cis-position. However, the splitting between these two bands may not be large and the broadening of the 840 cm^{-1} band might be due to two unresolved bands. Reaction of $[Rh(NS)Cl_2(PPh_3)]_2$

with triphenylphosphine gave a monomeric complex, $[Rh(NS)Cl_2(PPh_3)_2]$ which further corroborated the bridging nature of the NS group.

$$(PPh_3)Cl_2Rh \underset{\underset{\overset{N}{S}}{\big\backslash}}{\overset{\overset{S}{\overset{N}{\big/}}}{\Big\langle}} RhCl_2(PPh_3) \quad + \quad PPh_3$$

$$\xrightarrow[\text{reflux}]{CH_2Cl_2} \quad 2 \; Rh(NS)Cl_2(PPh_3)_2$$
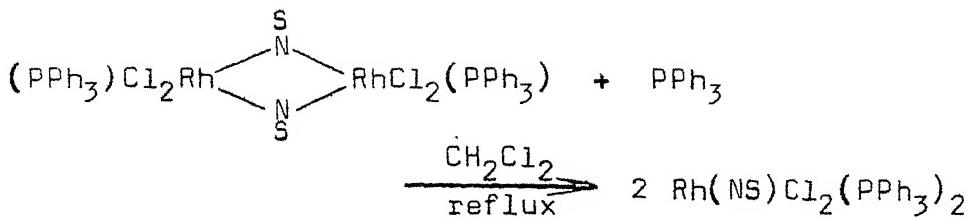
IR spectrum (Fig. III.I(2)) of $[Rh(NS)Cl_2(PPh_3)_2]$ showed a band around 1118 cm^{-1} due to terminal ν_{NS} and no band appeared at 840cm^{-1}. This was taken as an added evidence for the presence of bridging NS in $[Rh(NS)Cl_2(PPh_3)]_2$ which absorbed at 840 cm^{-1} due to bridge ν_{NS}.[12]

The reaction of $(NSCl)_3$ with $[Rh(NO)Cl_2(PPh_3)_2]$ and $[Rh(NO)Br_2(PPh_3)_2]$ at high temperature ($\sim 40^{\circ}C$) gave an air stable brown solid of empirical formula $[Rh(NS)Cl_2(PPh_3)]$ whose i.r. spectrum showed bands at 1120 cm^{-1} due to terminal, bent NS group and at 340 cm^{-1} and 265 cm^{-1} besides the characteristic bands of triphenylphosphine. The band at 340 cm^{-1} was assigned to ν_{Rh-Cl} (Cl trans to Cl) while the one, at 265 cm^{-1}, to ν_{Rh-Cl} (Cl trans to P; or to bridging chlorine modes or to both[31]). The molecular weight of $[Rh(NS)Cl_2(PPh_3)]_2$ in benzene was found to be 990 suggesting the dimeric nature of the complex (structure I).

$[Rh(NS)Cl_2(PPh_3)]_2$ reacted with triphenylphosphine to give red brown complex $[Rh(NS)Cl_2(PPh_3)_2]$ (structure II) whose i.r. spectrum showed all the bands similar to that of $[Rh(NS)Cl_2(PPh_3)]_2$ except the one at 265 cm^{-1}. This corroborated the presence of chlorobridges in $[Rh(NS)Cl_2(PPh_3)]_2$.
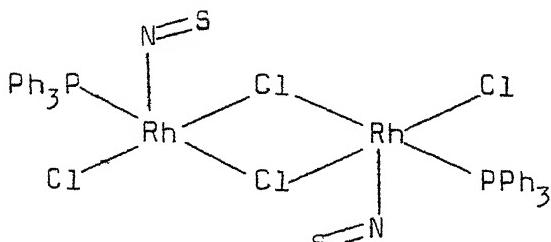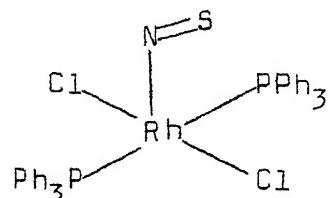
(I)   (II)

Reaction of $[Rh(CO)Cl(PPh_3)_2]$ with the limited amount of NSOH gave $[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$ while that with excess formed $[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$. The latter complex was also obtained by reacting $[RhCl(PPh_3)_3]$ with excess of NSOH. The diamagnetic complex $[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$ is stable, soluble in chloroform, dichloromethane, benzene and insoluble in hexane and ether having very low conductivity in nitrobenzene which ruled out its ionic character. Its i.r. spectrum (Fig. III.I(5)) showed absorption bands at 3400, 2100, 1630, 1118, 1060, 970, 930, 630 and 335 cm^{-1}, besides the characteristic bands of triphenylphosphine. The bands at 3400, 1630 and 930 cm^{-1} were assigned to the coordinated water molecule and the ones at 1118, 1060, 970 and 630 cm^{-1} to the characteristic bands of coordinated thiazate group.[32,33] The band

at 335 cm^{-1} was assigned to ν_{Rh-Cl}. The high frequency of ν_{CO} to its precursor (ν_{CO}, 1960 cm^{-1}) is reasonable for rhodium(III) system.

The reaction of excess NSOH with $[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$ and $[RhCl(PPh_3)_3]$ gave $[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$ whose i.r. spectrum (Fig. III.I(6)) was found to be exactly the same as that of $[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$ except the absence of bands at 2100 cm^{-1} and 335 cm^{-1} and the presence of band at 260 cm^{-1}. The band at 260 cm^{-1} was assigned to bridge ν_{Rh-Cl}. Its reaction with excess of triphenylphosphine in CH_2Cl_2 gave a brown complex, $[Rh(H_2O)(NSO)_2Cl(PPh_3)_2]$ whose far i.r. spectrum (Fig. III.I(7)) showed a new band at 335 cm^{-1}. No band was observed in the range 230-280 cm^{-1} which suggested the absence of chlorobridge in the compound. The dimeric and monomeric nature of $[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$ and $[Rh(H_2O)(NSO)_2Cl(PPh_3)_2]$ were corroborated by values of their molecular weights determined cryoscopically in benzene.

Our attempts to synthesize iridium nitrosyl complex, $[Ir(NO)Cl_2(PPh_3)_2]$, according to the literature method[34] have failed. In this reaction the end product was always found to be yellow crystalline complex, $[IrHCl_2(PPh_3)_3]$. Its i.r. spectrum (Fig. III.I(3)) and other properties exactly matched with the standard compound prepared previously by others.[35,36] The role of NO in the formation of $[IrHCl_2(PPh_3)_3]$ was not well understood. However, the possibility of its role as a catalyst might exist.

Reaction of trithiazyltrichloride with $[IrHCl_2(PPh_3)_3]$
gave a yellowish brown complex, $[Ir(NS)Cl_2(PPh_3)_2]$ whose i.r.
spectrum (Fig. III.I(4)) showed absorption band at 1120 cm^{-1}
besides the characteristic bands of triphenylphosphine. Band
at 1120 cm^{-1} was assigned to ν_{NS} which is in close agreement
with the one already reported for $[Ir(CO)(NS)Cl_2(PPh_3)_2]$
(ν_{NS}, 1115 cm^{-1}).[13] Its far i.r. spectrum showed band at
325 cm^{-1} due to ν_{Ir-Cl} (Cl trans to Cl).[37] The complex was
found to be diamagnetic suggesting iridium to be present in
+3 oxidation state. On the basis of the results thus
obtained from physicochemical studies, the following structure
(III) has been tentatively assigned to the complex:

(III)
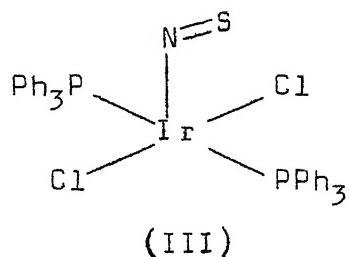
Table III.1. Analytical data of the complexes

Compound	ANALYSES Calculated (Found) %						
	C	H	N	S	Cl/Br	P	Rh
[Rh(NS)Cl$_2$(PPh$_3$)]$_2$	44.8 (44.7)	3.1 (3.0)	2.9 (3.0)	6.6 (6.7)	14.7 (14.9)	6.4 (6.5)	21.4 (21.2)
[Rh(NS)Cl$_2$(PPh$_3$)$_2$]	58.1 (58.0)	4.0 (3.9)	1.9 (2.0)	4.3 (4.4)	9.5 (9.4)	8.3 (8.2)	13.8 (13.6)
[Rh(CO)(H$_2$O)(NSO)$_2$Cl(PPh$_3$)]	39.9 (40.1)	3.0 (3.0)	4.9 (4.8)	11.2 (11.0)	6.3 (6.3)	5.4 (5.5)	18.0 (17.9)
[Rh(H$_2$O)(NSO)$_2$Cl(PPh$_3$)]$_2$	39.8 (39.9)	3.1 (3.2)	5.1 (4.9)	11.8 (11.7)	6.6 (6.4)	5.7 (5.8)	18.9 (18.7)
[Rh(H$_2$O)(NSO)$_2$Cl(PPh$_3$)$_2$]	53.7 (53.5)	4.0 (4.1)	3.5 (3.4)	7.9 (7.8)	4.5 (4.5)	7.7 (7.6)	12.8 (12.8)
[IrH Cl$_2$(PPh$_3$)$_3$]	61.7 (61.3)	4.4 (4.3)	– –	– –	6.8 (6.7)	8.9 (8.7)	– –
[Ir(NS)Cl$_2$(PPh$_3$)$_2$]	51.9 (51.5)	3.6 (3.5)	1.7 (1.8)	3.8 (3.7)	8.5 (8.6)	7.4 (7.5)	– –

Table III.2. Colour, melting point and important infrared frequencies of the complexes

Complexes	Colour	M.p. or (decomp.) in air (°C)	Molecular weight Calcd. (Found)	Infrared Frequencies		Other Frequencies (cm⁻¹)
				ν_{NS} (cm⁻¹)	ν_{M-X} (cm⁻¹)	
$[Rh(NS)Cl_2(PPh_3)]_2$	Brown	220	964 (900)	840	335	-
$[Rh(NS)Cl_2(PPh_3)]_2$	Brown	215	964 (990)	1120	340, 265	-
$[Rh(NS)Cl_2(PPh_3)_2]$	Brown	160	744 (710)	1118	335	-
$[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$	Greenish Brown	145(d)	570 (520)	-	335	3400, 2100, 1630, 1118, 1060, 970, 930, 630
$[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$	Brown	165-67	1084 (1010)	-	260	3400, 1630, 1118, 1060, 970, 930, 630
$[Rh(H_2O)(NSO)_2Cl(PPh_3)_2]$	Light Brown	153	804 (850)	-	335	3400, 1630, 1110, 1060, 970, 930, 630
$[IrHCl_2(PPh_3)_3]$	Yellow	185	-	-	325	2200
$[Ir(NS)Cl_2(PPh_3)_2]$	Yellowish Brown	148-50	-	1120	325	-

LEGEND TO THE FIGURES

Fig. III.I. Infrared Spectra of the Complexes in KBr/CsI
discs:

(1) $[Rh(NS)Cl_2(PPh_3)]_2$

(2) $[Rh(NS)Cl_2(PPh_3)_2]$

(3) $[IrHCl_2(PPh_3)_3]$

(4) $[Ir(NS)Cl_2(PPh_3)_2]$

(5) $[Rh(CO)(H_2O)(NSO)_2Cl(PPh_3)]$

(6) $[Rh(H_2O)(NSO)_2Cl(PPh_3)]_2$

(7) $[Rh(H_2O)(NSO)_2Cl(PPh_3)_2]$

INFRARED SPECTRA

Fig. III.I

INFRARED SPECTRA

Frequency cm^{-1} x 10^{-2}

% Transmittance (arb. scale)

(3)

(4)

% Transmittance (arb. scale)

Frequency, cm^{-1} x10^{-2}
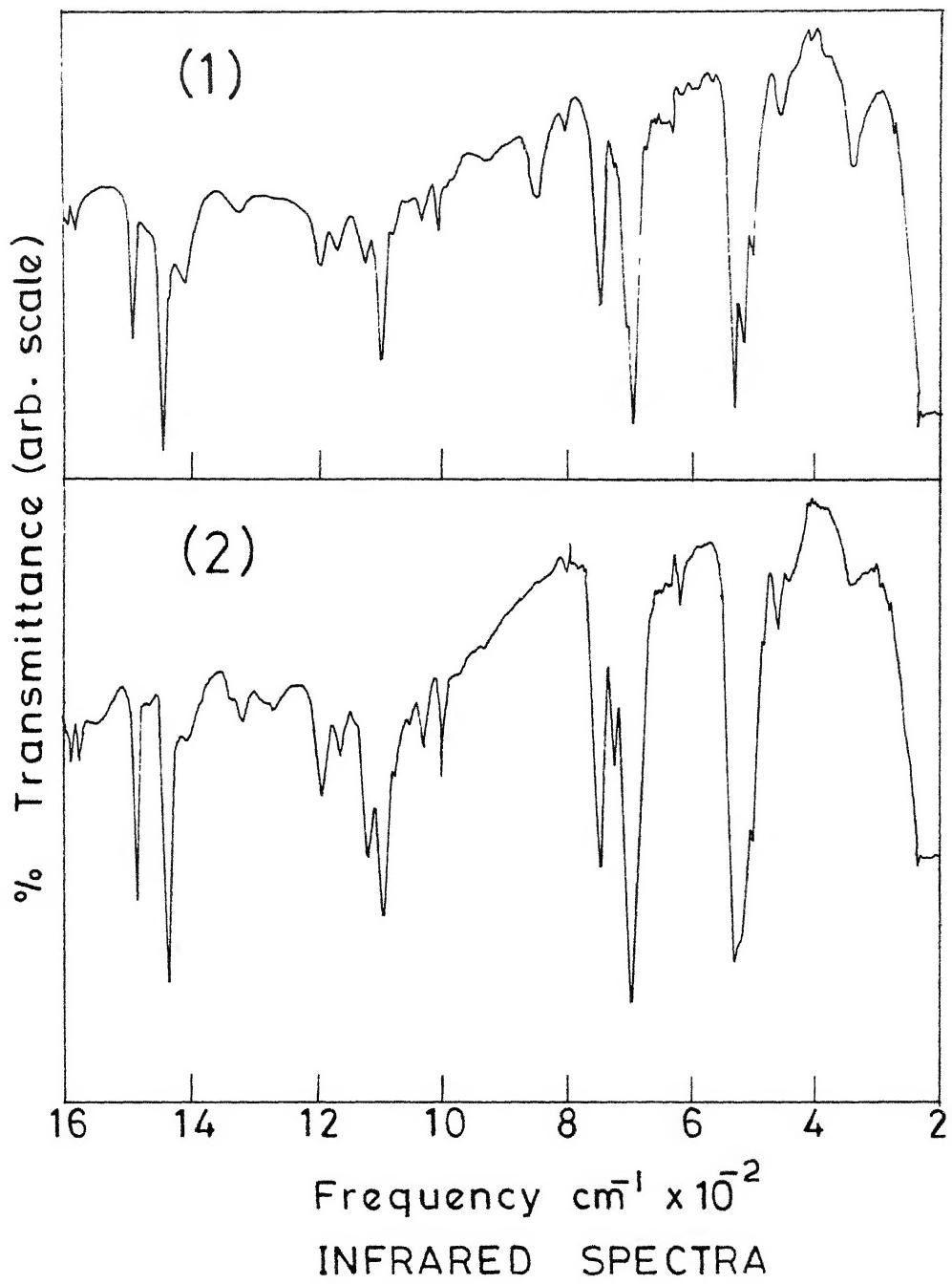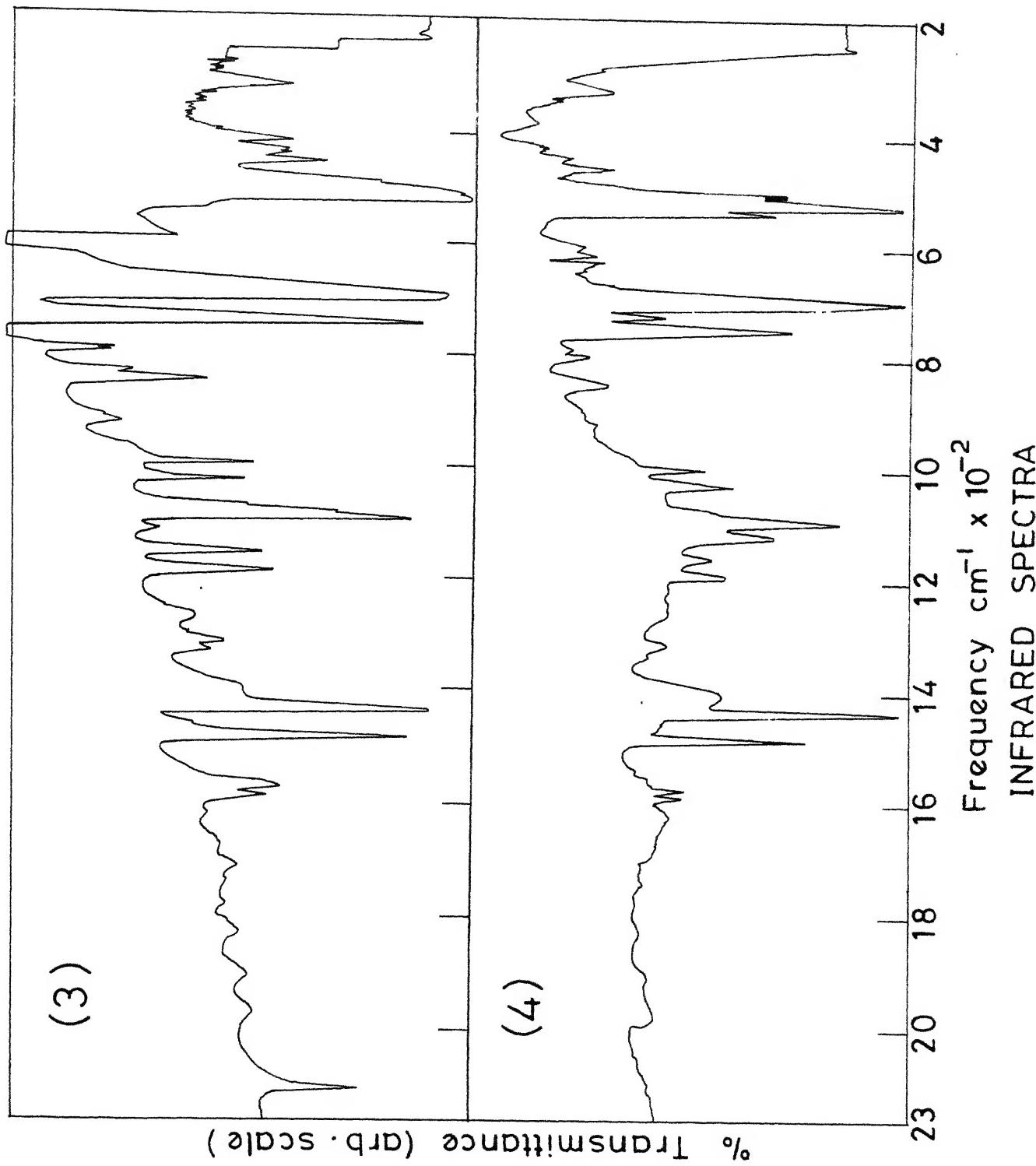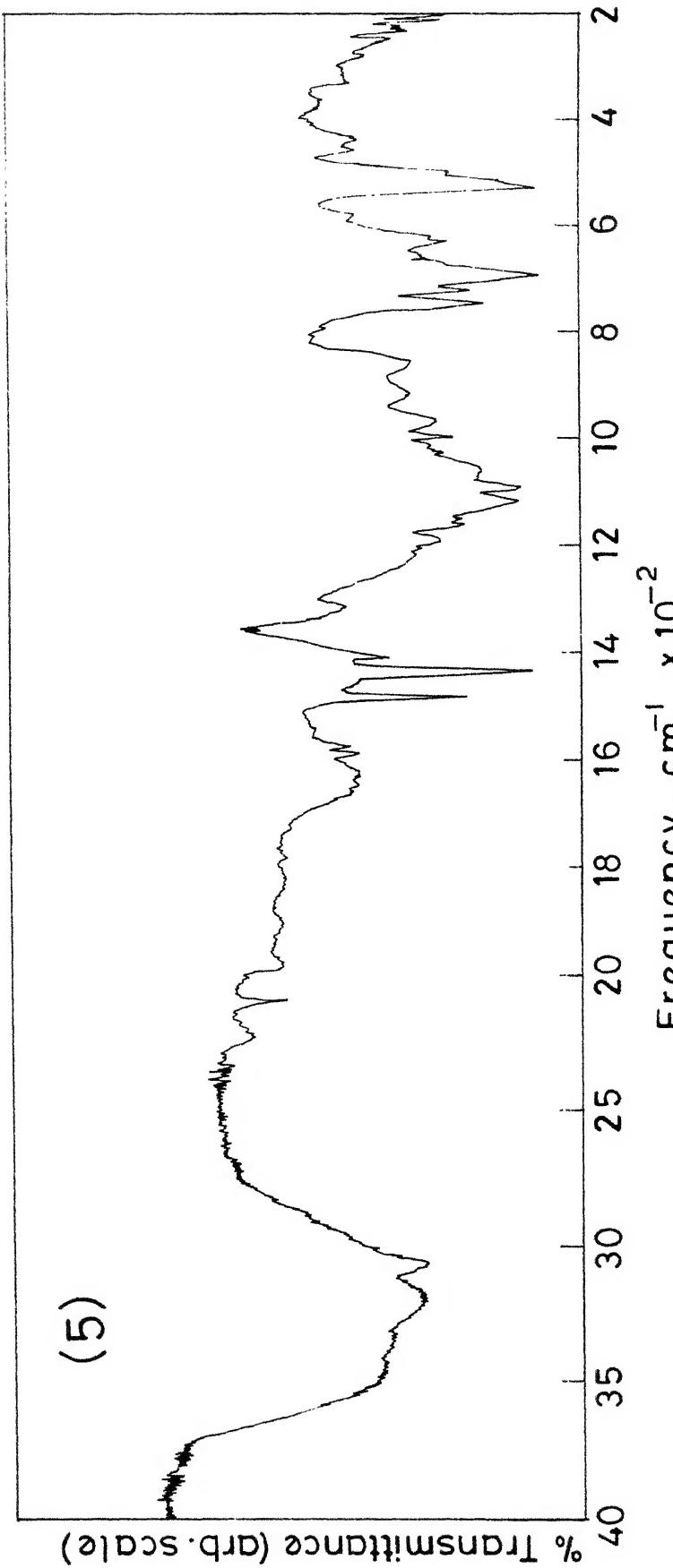
INFRARED SPECTRUM

Fig. III.1

(5)
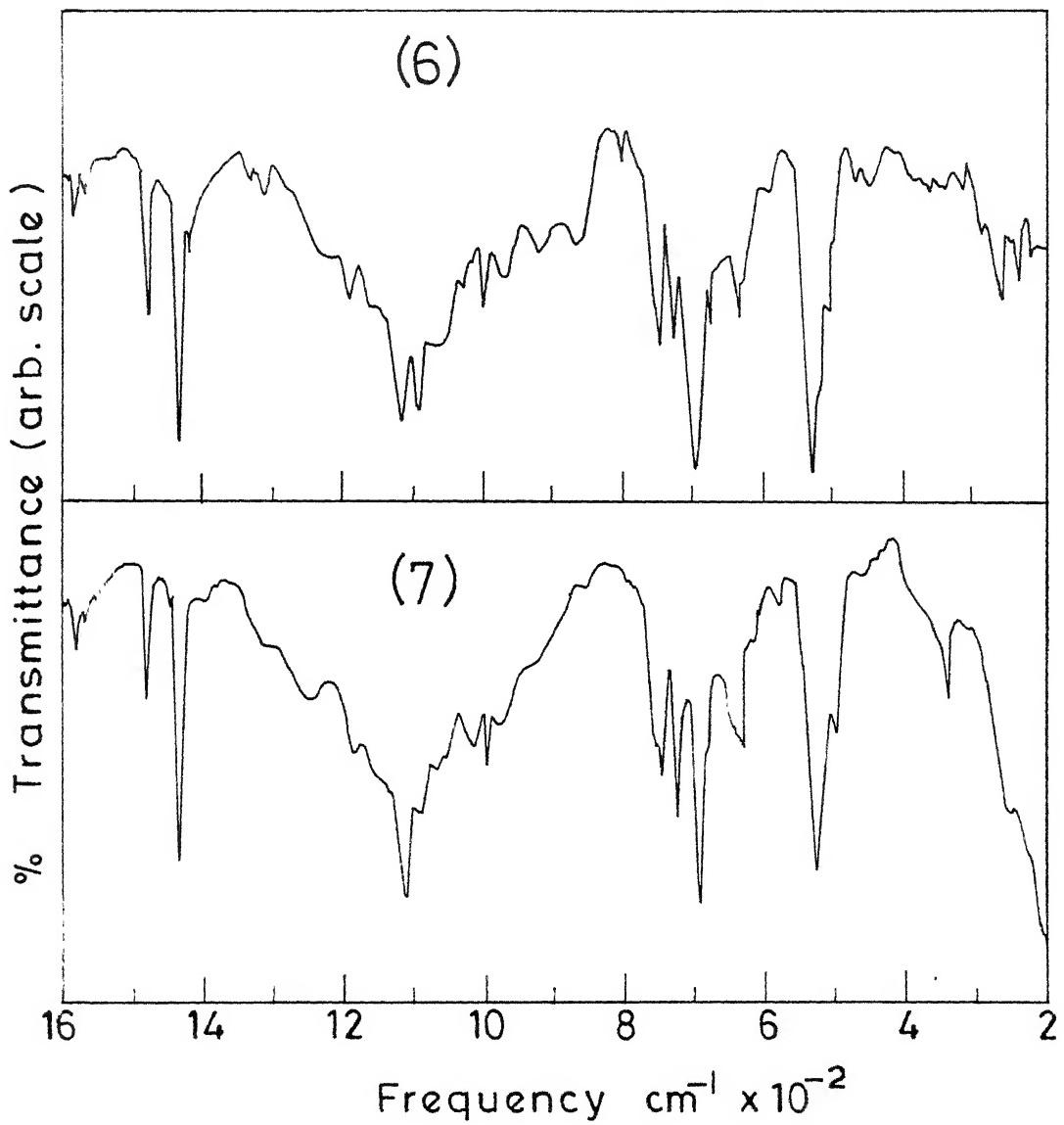
INFRARED SPECTRA

Fig. III . 1

REFERENCES

1. J. Chatt and J.R. Dilworth, J. Chem. Soc., Chem. Comm., 508 (1974).

2. M.W. Bishop, J. Chatt and J.R. Dilworth, J. Chem. Soc., Chem. Comm., 780 (1975).

3. M.W. Bishop, J. Chatt and J.R. Dilworth, J. Chem. Soc. Dalton Trans., I (1979).

4. B.W.S. Kolthammer and P. Legzdins, J. Am. Chem. Soc., 100, 2247 (1978).

5. K.K. Pandey and U.C. Agarwala, Z. Anorg. Allgem. Chem., 461(2), 231 (1980).

6. K.K. Pandey, K.C. Jain and U.C. Agarwala, Inorg. Chim. Acta, 48, 23 (1981).

7. K.C. Jain, K.K. Pandey, S.S. Katiyar and U.C. Agarwala, Internat. Conf. Coord. Chem., 440 (1980).

8. T.J. Greenhaugh, B.W.S. Kolthammer, P. Legzdins and J. Trotter, J. Chem. Soc., Chem. Comm., 1036 (1978).

9. M.B. Hursthouse and M. Motevalli, J.Chem.Soc.Dalton Trans., 1362 (1979).

10. T.J. Greenhough, B.W.S. Kolthamer, P. Legzdins and J. Trotter, Inorg. Chem., 18, 3548 (1979).

11. R. Grinter and J.D. Woollins, Inorg. Chim. Acta, 39, 193 (1980).

12. K.K. Pandey and U.C. Agarwala, Inorg. Chem., 20, 1308 (1981).

13. K.K. Pandey and U.C. Agarwala, Indian J. Chem., 20A, SCCA-2077 (1981).

14. C. Bottinger, Chem. Ber., 11, 1407 (1978).

15. P.W. Schenk, Chem. Ber., 75, 94 (1942).

16. W. Verbeek and W. Sundermeyer, Angew. Chem. Internat. Edn., $\underline{8}$, 376 (1969).

17. O.J. Scherer and P. Horning, Angew. Chem. Internat. Edn., $\underline{5}$, 729 (1966).

18. D.A. Armitage and M.J. Clark, J. Organomet. Chem., $\underline{24}$, 629 (1970).

19. D.A. Armitage and A.W. Sinden, J. Organomet. Chem., $\underline{44}$, C43 (1972).

20. W. Lidy and W. Sundermeyer, Z. Naturforsch., $\underline{29b}$, 276 (1974).

21. M. Becke-Goehring, R. Schwarz and W. Spiess, Z. Anorg. Allgem. Chem., $\underline{293}$, 294 (1958).

22. J.A. Osborn, F.H. Sardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, 1711 (1960).

23. J.A. Osborn and G. Wilkinson, Inorganic Synth., $\underline{10}$, 68 (1968).

24. N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorganic Synth., $\underline{15}$, 58 (174).

25. W.L. Jolly and K.D. Maguire, Inorg. Synths., $\underline{9}$, 102 (1967).

26. K.K. Pandey, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India (1981).

27. F.E. Beamish, A textbook of Analytical Chemistry of Noble Metals, Pergamon, Oxford (1966).

28. A.I. Vogel, A textbook of Quantitative Inorganic Analysis, 3rd Edn., Longmans Green, London (1961).

29. G. Schmid and G. Ritter, Chem. Ber., 3008 (1975).

30. G. Schmid and G. Ritter, Angew. Chem. Int. Ed. Eng., $\underline{14}$, 645 (1975).

31. D.M. Adams, Metal-Ligand and Related Vibrations, Edward Arnold, London (1967).

32. P.O. Tchir and R.D. Spratley, Can. J. Chem., 53, 2318
     (1975).

33. A.A. Bhattacharyya, A.G. Turner, Inorg. Chim. Acta, 44,
     L185 (1980).

34. G.R. Crooks and B.F.G. Johnson, J. Chem. Soc. (A), 1662
     (1970).

35. A. Araneo and S. Martinengo, Gazeta Chim. Italiana, 95,
     61 (1965).

36. L. Vaska and John W. Diluzio, J. Am. Chem. Soc., 84,
     4989 (1962); L. Vaska, J. Am. Chem. Soc., 83, 756 (1961).

37. G.L. Geoffroy and J.R. Lehman, Progress in Inorganic
     Chemistry and Radiochemistry, 20, 200 (1977).

INTERACTION OF NITROSYL CHLORIDE, NITROSYL BROMIDE,
NITROSYL TRIBROMIDE AND DINITROGENTRIOXIDE WITH:

I. $RuCl_3 \cdot xH_2O$ IN PRESENCE OF TRIPHENYLPHOSPHINE,
TRIPHENYLARSINE AND TRIPHENYLSTIBINE;

II. $[Ru(CO)_3(PPh_3)_2]$, $[RuHCl(CO)(PPh_3)_3]$,
$[RuCl_3(AsPh_3)_2 \cdot MeOH]$ and $[RuCl_2(PPh_3)_3]$.

Although ruthenium forms more nitrosyls than any other
element, in the last few years the balance has been somewhat
redressed from the point of view of number of nitrosyls of the
other elements prepared (though many of the new complexes are
of osmium and iridium and are analogues of known ruthenium
ones) means that the single element boundary is not restric-
tive either. Although new ruthenium complexes have been
obtained, new synthetic routes to the existing complexes
found,[1-8] ruthenium nitrosyls probably still occupy the
central place in the nitrosyl chemistry in general. Activation
of nitrosyl chloride in homogeneous system by metal complexes
has received considerable attention because of possible

synthetic applications as well as interest in the catalytic processes.[9-12]   Besides a few reports,[8,13] literature is almost devoid of the concerned synthetic applications of nitrosyl tribromide and dinitrogentrioxide with transition metal complexes. In this chapter reactions of nitrosyl chloride, nitrosyl bromide, nitrosyl tribromide and dinitrogentrioxide with $RuCl_3 \cdot xH_2O$ in presence of triphenylphosphine, triphenylarsine and triphenylstibine and with some ruthenium complexes $[Ru(CO)_3(PPh_3)_2]$, $[RuHCl(CO)(PPh_3)_3]$, $[RuCl_3(AsPh_3)_2 \cdot MeOH]$ are described. The structures of the resulting nitrosyl, nitronitrato and carbonyl complexes have been proposed on the basis of i.r., magnetic measurements, elemental analyses, conductivity measurements and chemical reactions.

EXPERIMENTAL SECTION

All the chemicals used were of chemically pure or analar grade. All solvents were dried by standard procedures, distilled and deaerated just prior to use. Wherever necessary an atmosphere of purified argon was used.

Dichlorotris-(triphenylphosphine)ruthenium(II), tricarbonylbis(triphenylphosphine)ruthenium(0), carbonylchlorohydridotris(triphenylphosphine)ruthenium(II), trichlorobis-(triphenylarsine)ruthenium(III) methanol, nitrosyl chloride, nitrosyl bromide, nitrosyl tribromide, dinitrogentrioxide were prepared according to the methods described in the literature.[17-23]

(i) Reaction of NOCl with RuCl$_3$.xH$_2$O in presence of triphenyl-
phosphine

10 ml of an alcoholic solution of RuCl$_3$.xH$_2$O (0.2 g)
was added with stirring to a hot ethanol solution (20 ml) of
PPh$_3$ (1.2 g), followed by saturated NOCl solution (20 ml) in
CH$_2$Cl$_2$. On stirring vigorously, orange glistening crystals
of [Ru(NO)Cl$_3$(PPh$_3$)$_2$] were separated out which were centri-
fuged, washed with ethanol, ether and dried in vacuum (yield,
90 %).

(ii) Reaction of NOCl with RuCl$_3$.xH$_2$O in presence of triphenyl-
arsine

10 ml of an ethanolic solution of RuCl$_3$.xH$_2$O (0.12 g)
was added with stirring to a hot ethanol solution (20 ml) of
triphenylarsine (0.8 g), followed by saturated NOCl solution
(10 ml) in CH$_2$Cl$_2$. On stirring vigorously, orange glistening
crystals of [Ru(NO)Cl$_3$(AsPh$_3$)$_2$] were separated out which were
centrifuged, washed with ethanol, ether and dried in vacuum.

(iii) Reaction of NOCl with RuCl$_3$.xH$_2$O in presence of triphenyl-
stibine

20 ml of an ethanolic solution of RuCl$_3$.xH$_2$O (0.2 g)
was added with stirring to a hot ethanol solution (20 ml) of
SbPh$_3$ (1.2 g), followed by saturated NOCl solution (10 ml) in
CH$_2$Cl$_2$. On stirring vigorously, a mixture of compounds
[RuCl$_3$(SbPh$_3$)$_3$] and [Ru(NO)Cl$_3$(SbPh$_3$)$_2$] was obtained.

(iv) Reaction of NONO$_2$ with RuCl$_3$.xH$_2$O in presence of triphenyl-
    phosphine

    (a) An ethanolic solution (10 ml) of RuCl$_3$.xH$_2$O (0.14 g)
was added with stirring to a hot ethanol solution of triphenyl-
phosphine (0.8 g), followed by saturated solution (20 ml) of
NONO$_2$ in dichloromethane. On stirring vigorously, orange
crystals of [Ru(NO)Cl$_3$(PPh$_3$)$_2$] were obtained which were centri-
fuged, washed with ethanol, ether and dried in vacuum.

    (b) The same compound [Ru(NO)Cl$_3$(PPh$_3$)$_2$] was obtained
when NONO$_2$ was taken in benzene medium.

(v) Reaction of NOBr with RuCl$_3$.xH$_2$O in presence of triphenyl-
    phosphine

    An ethanolic solution (20 ml) of RuCl$_3$.xH$_2$O (0.2 g)
was added with stirring to a hot ethanol solution of triphenyl-
phosphine (1.2 g), followed by (ca. 2 M) NOBr solution (10 ml)
in dichloromethane. On stirring vigorously, orange glistening
crystals of [Ru(NO)Cl$_2$Br(PPh$_3$)$_2$] were obtained which were
centrifuged, washed with ethanol, ether and dried in vacuum.

(vi) Reaction of NOBr with RuCl$_3$.xH$_2$O in presence of triphenyl-
    arsine

    Reaction was performed exactly in a similar way as that
given for [Ru(NO)Cl$_2$Br(PPh$_3$)$_2$] except that 20 ml hot ethanolic
solution of triphenylarsine was used in place of triphenyl-

phosphine. Shining orange crystals of $[Ru(NO)Cl_2Br(AsPh_3)_2]$ were obtained.

(vii) Reaction of NOBr with $RuCl_3.xH_2O$ in presence of triphenylstibine

An ethanolic solution (10 ml) of $RuCl_3.xH_2O$ (0.14 g) was added with stirring to a hot ethanolic solution of triphenylstibine (0.8 g), followed by saturated NOBr (10 ml) solution in dichloromethane. Reaction mixture was further stirred for 10 minutes and kept on water bath for 10 minutes. A mixture of compounds $[Ru(NO)Cl_2Br(SbPh_3)_2]$ and $[RuCl_2Br(SbPh_3)_3]$ was obtained. The mixture was centrifuged, washed with ethanol, ether and dried in vacuum.

(viii) Reaction of $NOBr_3$ with $RuCl_3.xH_2O$ in presence of triphenylphosphine

10 ml of an ethanolic solution of $RuCl_3.xH_2O$ (0.2 g) was added with stirring to a hot ethanolic solution (20 ml) of PPh_3 (1.2 g), followed by 10 ml of freshly prepared $NOBr_3$ solution (ca. 2 M) in dichloromethane. On stirring vigorously and concentrating on water bath, orange brown crystals of $[Ru(NO)ClBr_2(PPh_3)_2]$ were separated out which were centrifuged, washed with methanol, ether and dried in vacuum.

(ix) Reaction of $NOBr_3$ with $RuCl_3.xH_2O$ in presence of triphenylarsine

Reaction was performed by the procedure similar to that given for $[Ru(NO)ClBr_2(PPh_3)_2]$ except that 20 ml hot ethanolic solution of triphenylarsine was added in place of

triphenylphosphine. Orange crystals of $[Ru(NO)ClBr_2(AsPh_3)_2]$ were obtained.

(x) Reaction of $NOBr_3$ with $RuCl_3 \cdot xH_2O$ in presence of triphenyl-stibine

An ethanolic solution (10 ml) of $RuCl_3 \cdot xH_2O$ (0.14 g) was added with stirring to a hot ethanolic solution of triphenyl-stibine (0.8 g), followed by 10 ml of $NOBr_3$ solution (ca. 2 M) in dichloromethane. It was further stirred for 10 minutes. Reddish brown crystals of $[RuClBr_2(SbPh_3)_3]$ were separated out which were centrifuged, washed with ethanol, hexane and dried in vacuum.

(xi) Reaction of $NONO_2$ with $RuCl_3 \cdot xH_2O$ in presence of triphenyl-arsine

An ethanolic solution (10 ml) of $RuCl_3 \cdot xH_2O$ (0.14 g) was added with stirring to a hot ethanolic solution (20 ml) of tri-phenylarsine (0.8 g), followed by 20 ml of saturated solution of dinitrogentrioxide in dichloromethane or benzene. The solu-tion, thus obtained, was vacuum concentrated, whereby orange crystals of $[Ru(NO)Cl_3(AsPh_3)_2]$ were separated out which were centrifuged, washed with ethanol, hexane and dried in vacuum.

(xii) Reaction of $NONO_2$ with $RuCl_3 \cdot xH_2O$ in presence of triphenyl-stibine

Reaction was carried out by a procedure similar to that given for $[Ru(NO)Cl_3(AsPh_3)_2]$ except that 20 ml hot ethanolic

solution of triphenylstibine was used in place of triphenyl-arsine. Red needle shaped crystals of $[RuCl_2(SbPh_3)_3]$ were separated which were centrifuged, washed with small amounts of ethanol, hexane and dried under vacuum.

(xiii) Reactions of NOCl, NOBr and NOBr$_3$ with RuCl$_2$(PPh$_3$)$_3$

Saturated solution of NOCl in CH_2Cl_2 (10 ml) was added to a solution (20 ml) of 0.2 g of $[RuCl_2(PPh_3)_3]$ in CH_2Cl_2. The resulting solution was stirred for 10 minutes followed by its vacuum concentration. Hot methanol (20 ml) was added to the concentrated solution whereby shining orange crystals of $[Ru(NO)Cl_3(PPh_3)_2]$ were separated which were centrifuged, washed with ethanol, ether and dried in vacuum. On addition of dichloromethane solution of NOBr and NOBr$_3$ in place of NOCl and following the procedure noted above,$[Ru(NO)Cl_2Br(PPh_3)_2]$ was obtained.

(xiv) Reaction of RuCl$_3$(AsPh$_3$)$_2$.MeOH with NOCl, NOBr and NOBr$_3$

RuCl$_3$(AsPh$_3$)$_2$.MeOH (0.2 g) was dissolved in 10 ml CH_2Cl_2 and 10 ml saturated solution of NOCl in CH_2Cl_2 was added and stirred for 10 minutes. The resulting solution was vacuum concentrated and cold pentane (50 ml) was added to the concen-trated solution whereby yellowish orange powder of $[Ru(NO)Cl_3$-$(AsPh_3)_2]$ was separated which was centrifuged, washed with pentane and dried in vacuum. On addition of dichloromethane solution of NOBr and NOBr$_3$ in place of NOCl and following the

procedure noted above $[Ru(NO)Cl_2Br(AsPh_3)_2]$ was obtained.

(xv) Reactions of NOCl with $[Ru(CO)_3(PPh_3)_2]$ and $[RuHCl(CO)(PPh_3)_3]$

20 ml solution of NOCl in CH_2Cl_2 was mixed with a solution (10 ml) of $[Ru(CO)_3(PPh_3)_2]$ (0.5 g) in CH_2Cl_2 to which 40 ml of hot methanol was added. On vigorous stirring, orange glistening crystals of $[Ru(NO)Cl_3(PPh_3)_2]$ (yield, 80%) were separated out which were centrifuged immediately, washed with methanol, ether and dried in vacuum. On keeping the centrifugate for 3-4 hr, a white compound, $[Ru(CO)_2Cl_2(PPh_3)_2]$ was separated out which was centrifuged, washed with methanol, ether and dried in vacuum (yield, 10%).

The same compounds were obtained when $[RuHCl(CO)(PPh_3)_3]$ was used as a starting material in place of $[Ru(CO)_3(PPh_3)_2]$ but the yield of dicarbonyl, $[Ru(CO)_2Cl_2(PPh_3)_2]$ obtained was only about 4%.

The reaction products were the same if dichloromethane was substituted by benzene as the reaction medium.

(xvi) Reactions of NOBr with $[Ru(CO)_3(PPh_3)_2]$ or $[RuHCl(CO)-(PPh_3)_3]$

The procedure for the reaction was same as that given in (xv) except that a solution (ca. 2 M) of NOBr was used in place of NOCl. The reaction with $[Ru(CO)_3(PPh_3)_2)]$ gave orange brown plates of $[Ru(NO)Br_3(PPh_3)_2]$ (yield, 40%), while

that with $[RuHCl(CO)(PPh_3)_2]$, orange plate type crystals of $[Ru(NO)ClBr_2(PPh_3)_2]$ (yield, 40%.) and a white compound $[Ru(CO)_2Br_2(PPh_3)_2]$ (yield, ca. 10%.) were obtained.

(xvii) Reactions of $NOBr_3$ with $[Ru(CO)_3(PPh_3)_2]$ or $[RuHCl(CO)-(PPh_3)_3]$

The procedures for the reactions of $NOBr_3$ with $[Ru(CO)_3-(PPh_3)_2]$ or $[RuHCl(CO)(PPh_3)_3]$ were same as these given in (xvi). Both $[Ru(CO)_3(PPh_3)_2]$ and $[RuHCl(CO)(PPh_3)_3]$ gave $[Ru(NO)Br_3(PPh_3)_2]$ (yield, ca. 20%.) and $[Ru(CO)_2Br_2(PPh_3)_2]$ (yield, ca. 50%. with $[Ru(CO)_3(PPh_3)_2]$ and ca. 20%. with $[RuHCl(CO)(PPh_3)_3]$).

(xviii) Reactions of N_2O_3 with $[Ru(CO)_3(PPh_3)_2]$ or $[RuHCl(CO)-(PPh_3)_3]$

A saturated solution (20 ml) of $NONO_2$ in CH_2Cl_2 was added to 10 ml solution of $[Ru(CO)_3(PPh_3)_2]$ (0.5 g) in CH_2Cl_2. The reaction mixture was concentrated on a water bath and 50 ml of hot methanol was added to it. On keeping the reaction mixture overnight, an orange yellow compound $[Ru(NO_2)(NO_3)(CO)_2-(PPh_3)_2]$ was obtained which was centrifuged, washed with methanol, ether and dried in vacuum.

Carbon, hydrogen, nitrogen, phosphorus, arsenic and halogen analyses, melting point, infrared spectra and magnetic measurements were carried out according to the methods given in Chapter II. The results of these studies are given in Tables IV.1 and IV.2. All compounds except the mixtures

obtained in stibine case were found to be diamagnetic.

RESULTS AND DISCUSSION

The analytical data of the complexes suggested their compositions as proposed in Table IV.1. Further their diamagnetic behaviour, except $RuClBr_2(SbPh_3)_3$, along with the charge balance indicated that ruthenium in these complexes is in the +2 oxidation state. The compounds were found to be non-conducting in nitrobenzene which rules out the possibility of their ionic nature. Although compounds $[Ru(NO)Cl_3L_2]$ (L = PPh_3 or $AsPh_3$) and $[Ru(NO)ClBr_2L_2]$ have been prepared previously[26-28] by two step process, the procedure developed by us involves simply the reaction of the metallic salt solution with NOX (X = Cl, Br, Br_3 or NO_2) in the presence of triphenylphosphine or triphenylarsine. The compounds were synthesized in pure state in about 80%. yield. The i.r. spectra showed the positions of $\nu_{NO}+$ for the ruthenium nitrosyl halide complexes in the range 1825 - 1876 cm^{-1} which are in close agreement with the values reported previously[26-28] (Fig. IV.I(1-4)). The presence of coordinated NO as NO^+ in these complexes has also been supported by X-ray studies[29] where the angle Ru-N-O was found to be 180°. In addition, infrared frequencies ν_{NO}° corrected according to the Iber's rule, were greater than 1620 cm^{-1}. These six coordinated nitrosyl complexes can, thus, be classified as linear, $\{RuNO\}^6$ type[24,25] having ruthenium in +2 oxidation state. The metal to nitrosyl bond could be

considered as formed by donation of σ-electrons from nitrogen to metal and back donation from the filled metal d-orbitals to those of $\pi^*(NO)$. Generally, in $\{RuNO\}^6$ type of complexes, NO is a good trans directing ligand[28] and in complexes, $[Ru(NO)X_3-L_2]$ (X = Cl or Br; L = tertiaryphosphine, arsine or stibine) X is present invariably trans to NO.[28] Replacement of the X ligand in these complexes was found to be relatively facile.[30,31] Further in some of the $[RuXY_2L_2(NO)]$ type complexes, X, the weakest trans directing ligand was found to be trans to NO.[28] On the basis of these arguments applicable for $\{RuNO\}^6$, the following geometries are tentatively assigned to the resulting complexes (structure I and II).

(I)   (II)
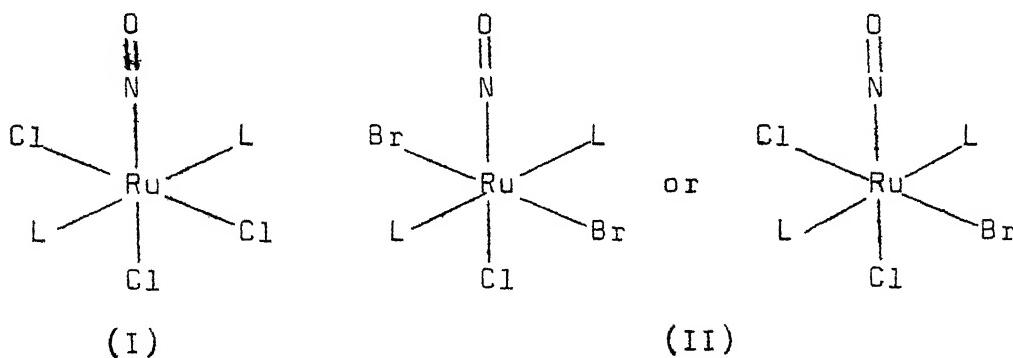
Although the reactions of NOX (X = Cl, Br, Br_3 or NO_2) with $RuCl_3 \cdot xH_2O$ in presence of $SbPh_3$ led to the formation of $[RuCl_3(SbPh_3)_3]$, $[RuCl_2Br(SbPh_3)_3]$, $[RuClBr_2(SbPh_3)_3]$ and $[RuCl_2(SbPh_3)_3]$, the complexes $[RuCl_3(SbPh_3)_3]$ and $[RuCl_2Br-(SbPh_3)_3]$ could not be isolated in the pure state. These were contaminated with $[Ru(NO)Cl_3(SbPh_3)_2]$ (ν_{NO}, 1832 cm^{-1}) and

$[Ru(NO)Cl_2Br(SbPh_3)_2]$ (ν_{NO}, 1825 cm^{-1}) respectively. The impure compounds were found to be slightly paramagnetic and nonelectrolytes. The structure of $RuCl_2(SbPh_3)_3$ is five coordinated with a vacant octahedral site about the square-pyramidal configuration being effectively blocked by a phenyl ring.[32] Contamination of Ru(III) complexes as impurities in the above complexes of tertiarystibine, corroborates the fact that tertiary stibine is less reducing as compared to tertiary-arsines and phosphines.

The reactions of $NONO_2$ with $RuCl_3 \cdot xH_2O$ in presence of PPh_3, $AsPh_3$ and $SbPh_3$ gave consistently Ru(II) compounds indicating reducing nature of $NONO_2$.

Reactions of NOX (X = Cl, Br or Br_3) with $[Ru(CO)_3(PPh_3)_2]$ and $[RuHCl(CO)(PPh_3)_3]$ gave nitrosyls of the type $[RuX_3(NO)-(PPh_3)_2]$ as a major product together with dicarbonyl complexes, $[Ru(CO)_2X_2(PPh_3)_2]$. It will be interesting to observe that the percentage yield of the nitrosyl complexes vary with the stability of NOX in CH_2Cl_2 (NOCl > NOBr > $NOBr_3$)[17-19] while that of dicarbonyl complexes in the reverse order. It could possibly be related to the time for which NO remains in solution.

Generally trans-$[Ru(CO)_2X_2(PPh_3)_2]$ are pale yellow to yellow coloured[29,33] while cis-isomers are white and relatively more stable. Since all the prepared dicarbonyls were white, it is tactly presumed that $[Ru(CO)_2Cl_2(PPh_3)_2]$ should be having

cis-configuration. Since the melting point $(259-60^\circ C)$ and
the position of the ν_{CO} bands $(2064 \text{ cm}^{-1}$ and $2001^{-1})$ of
$[Ru(CO)_2Cl_2(PPh_3)_2]$ correspond to those of the already prepared
one having the cis-geometry (structure III),[34] the same cis-
geometry is assigned to $[Ru(CO)_2Cl_2(PPh_3)_2]$.

Since the melting point $(233^\circ C)$ and the position of ν_{CO}
bands $(2040 \text{ cm}^{-1}$, 1980 cm^{-1} and a shoulder at $1950 \text{ cm}^{-1})$ of
the white complex differ from the m.p. $(270^\circ C)$ and the posi-
tions of ν_{CO} $(2061 \text{ cm}^{-1}$ and $1980 \text{ cm}^{-1})$ of one of the known
cis-$[RuBr_2(CO)_2(PPh_3)_2]$ (structure IV),[35] it is assumed that the
dicarbonyl,$[RuBr_2(CO)_2(PPh_3)_2]$ did not have the cis-geometry
given in structure IV. Consequently one of the remaining
cis-geometries shown in structure V could possibly be assigned
to $[Ru(CO)_2Br_2(PPh_3)_2]$.

CO
OC   PPh₃
     Ru
Ph₃P   Cl
        Cl

(III)

CO
OC   PPh₃
     Ru
Ph₃P   Br
        Br

(IV)

CO
OC   PPh₃
     Ru
Br   PPh₃
        Br

or

Br
OC   PPh₃
     Ru
OC   PPh₃
        Br

(V)
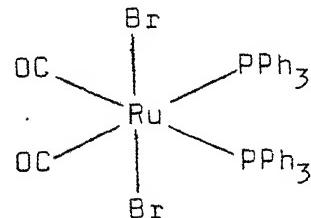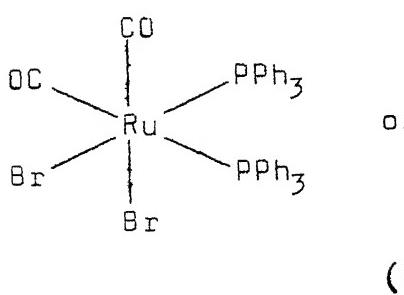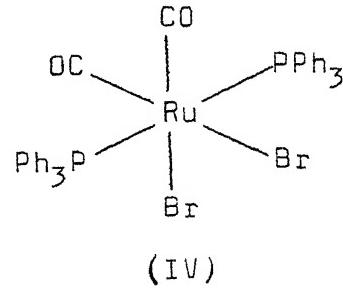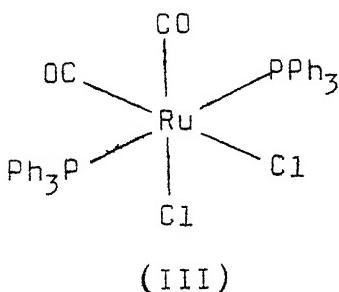
Interaction of dinitrogentrioxide with $[Ru(CO)_3(PPh_3)_2]$ or $[RuHCl(CO)(PPh_3)_3]$ yielded N-bonded nitro-nitrato complex $[Ru(NO_2)(NO_3)(CO)_2(PPh_3)_2]$ as indicated by the characteristic bands of NO_2^- (1390, 1317, 825 cm^{-1}) and NO_3^- (1494, 1270, 995 cm^{-1}). A very small peak at 1873 cm^{-1} was also observed in the i.r. spectrum of the above compound which indicated the presence of trace amounts of $[Ru(NO)(NO_3)_3(PPh_3)_2]$. Formation of NO_2^- ligand as N-bonded rather than O-bonded is supported by the presence of the characteristic band of N-bonded NO_2^- in the region of 1317 cm^{-1}. This should not have been present if the NO_2^- is O-bonded.[37-39]

Table IV.1. Analytical data of the complexes

Complexes	ANALYSES Calculated (Found) %				
	C	H	N	Cl/Br	P/As
1	2	3	4	5	6
[Ru(NO)Cl₃(PPh₃)₂]	56.8 (56.6)	3.9 (4.0)	1.8 (2.0)	13.9 (14.2)	8.1 (7.9)
[Ru(NO)Cl₂Br(PPh₃)₂]	53.6 (53.3)	3.7 (3.9)	1.7 (1.8)	18.7 (18.6)	7.7 (7.5)
[Ru(NO)ClBr₂(PPh₃)₂]	50.8 (50.7)	3.5 (3.5)	1.6 (1.5)	23.0 (22.9)	7.3 (7.2)
[Ru(NO)Br₃(PPh₃)₂]	48.3 (48.1)	3.3 (3.5)	1.6 (1.5)	26.8 (26.5)	6.9 (7.0)
[Ru(NO)Cl₃(AsPh₃)₂]	50.8 (50.4)	3.5 (3.2)	1.6 (1.5)	12.5 (12.7)	17.6 (17.8)
[Ru(NO)Cl₂Br(AsPh₃)₂]	48.3 (48.4)	3.3 (3.3)	1.5 (1.7)	16.8 (16.9)	16.7 (16.6)
[Ru(NO)ClBr₂(AsPh₃)₂]	46.0 (46.1)	3.2 (3.0)	1.5 (1.6)	20.8 (21.0)	15.9 (15.7)
[RuClBr₂(SbPh₃)₃]	47.7 (47.9)	3.3 (3.5)	-- --	14.4 (14.5)	-- --

Table IV.1 (contd.)

1	2	3	4	5	6
$[RuCl_2(SbPh_3)_3]$	52.6 (52.3)	3.6 (3.7)	– –	5.7 (6.0)	– –
$[Ru(CO)_2Cl_2(PPh_3)_2]$	60.6 (60.7)	4.0 (3.9)	– –	9.4 (9.6)	8.2 (8.0)
$[Ru(CO)_2Br_2(PPh_3)_2]$	54.2 (54.3)	3.6 (3.8)	– –	19.0 (19.2)	7.4 (7.5)
$[Ru(NO_2)(NO_3)(CO)_2(PPh_3)_2]$	57.8 (57.0)	3.8 (3.5)	3.5 (3.8)	– –	7.8 (7.6)

Table IV.2. Colour, melting point and important infrared frequencies of the complexes

Complexes	Colour	M.P. (°C)	ν_{NO} (cm⁻¹)	ν_{CO} (cm⁻¹)	ν_{NO_2} (cm⁻¹)	ν_{NO_3} (cm⁻¹)
			Infrared Frequencies		Other	
$[Ru(NO)Cl_3(PPh_3)_2]$	Orange	240–2	1876	-	-	-
$[Ru(NO)Cl_2Br(PPh_3)_2]$	Orange	238	1874	-	-	-
$[Ru(NO)ClBr_2(PPh_3)_2]$	Brown orange	235	1874	-	-	-
$[Ru(NO)Br_3(PPh_3)_2]$	Brown orange	230	1873	-	-	-
$[Ru(NO)Cl_3(AsPh_3)_2]$	Yellowish orange	>280	1874	-	-	-
$[Ru(NO)Cl_2Br(AsPh_3)_2]$	Orange	>280	1875	-	-	-
$[Ru(NO)ClBr_2(AsPh_3)_2]$	Orange	>280	1873	-	-	-
$[RuClBr_2(SbPh_3)_3]$	Yellowish red	190–3	-	-	-	-
$[RuCl_2(SbPh_3)_3]$	Red	>230	-	-	-	-
$[Ru(CO)_2Cl_2(PPh_3)_2]$	White	257–9	-	2001, 2064	-	-
$[Ru(CO)_2Br_2(PPh_3)_2]$	White	233	-	1980, 2040	-	-
$[Ru(CO)_2(NO_2)(NO_3)(PPh_3)_2]$	Orange yellow	171–2	-	-	1390, 1317, 825	1494, 1270, 995

LEGEND TO THE FIGURES

Fig. IV.I. Infrared Spectra of the Complexes in KBr discs:

(1) $[RuCl_2(SbPh_3)_3]$

(2) $[Ru(NO)Cl_3(SbPh_3)_2]$ and $[RuCl_3(SbPh_3)_3]$

(3) $[Ru(NO)Cl_3(PPh_3)_2]$

(4) $[Ru(NO)Cl_3(AsPh_3)_2]$

(5) $[Ru(CO)_2Br_2(PPh_3)_2]$

(6) $[Ru(CO)_2Cl_2(PPh_3)_2]$

(7) $[Ru(NO_2)(NO_3)(CO)_2(PPh_3)_2]$

% Transmittance (arb. scale)

(1)

(2)

Frequency cm^{-1} x 10^{-2}
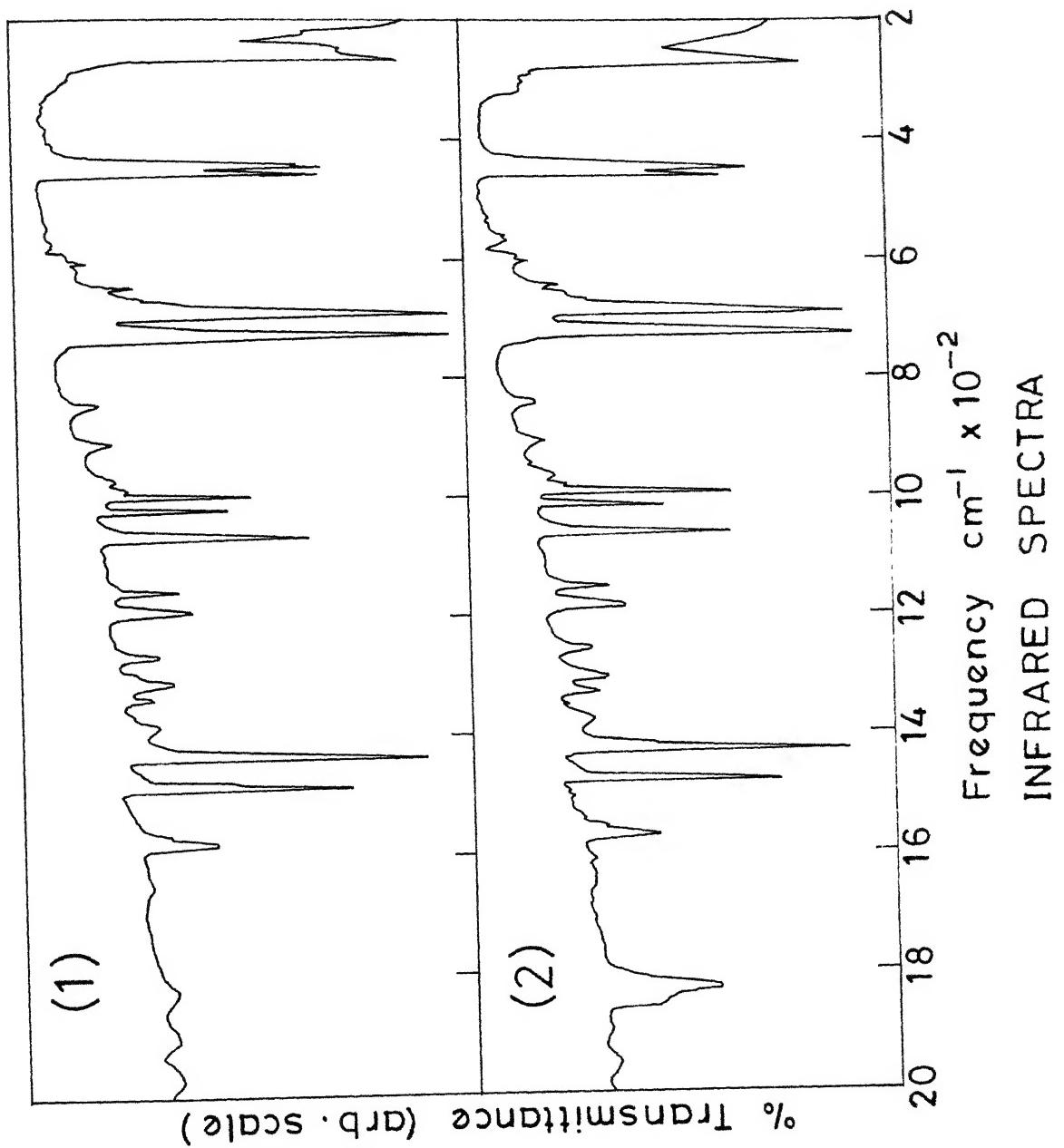
INFRARED SPECTRA

Fig. IV.1

INFRARED SPECTRA

Fig. IV.I

INFRARED SPECTRA

Fig. IV. I

% Transmittance (arb. scale)

Frequency cm^{-1} x 10^{-2}

INFRARED SPECTRUM

Fig.IV.I

(7)
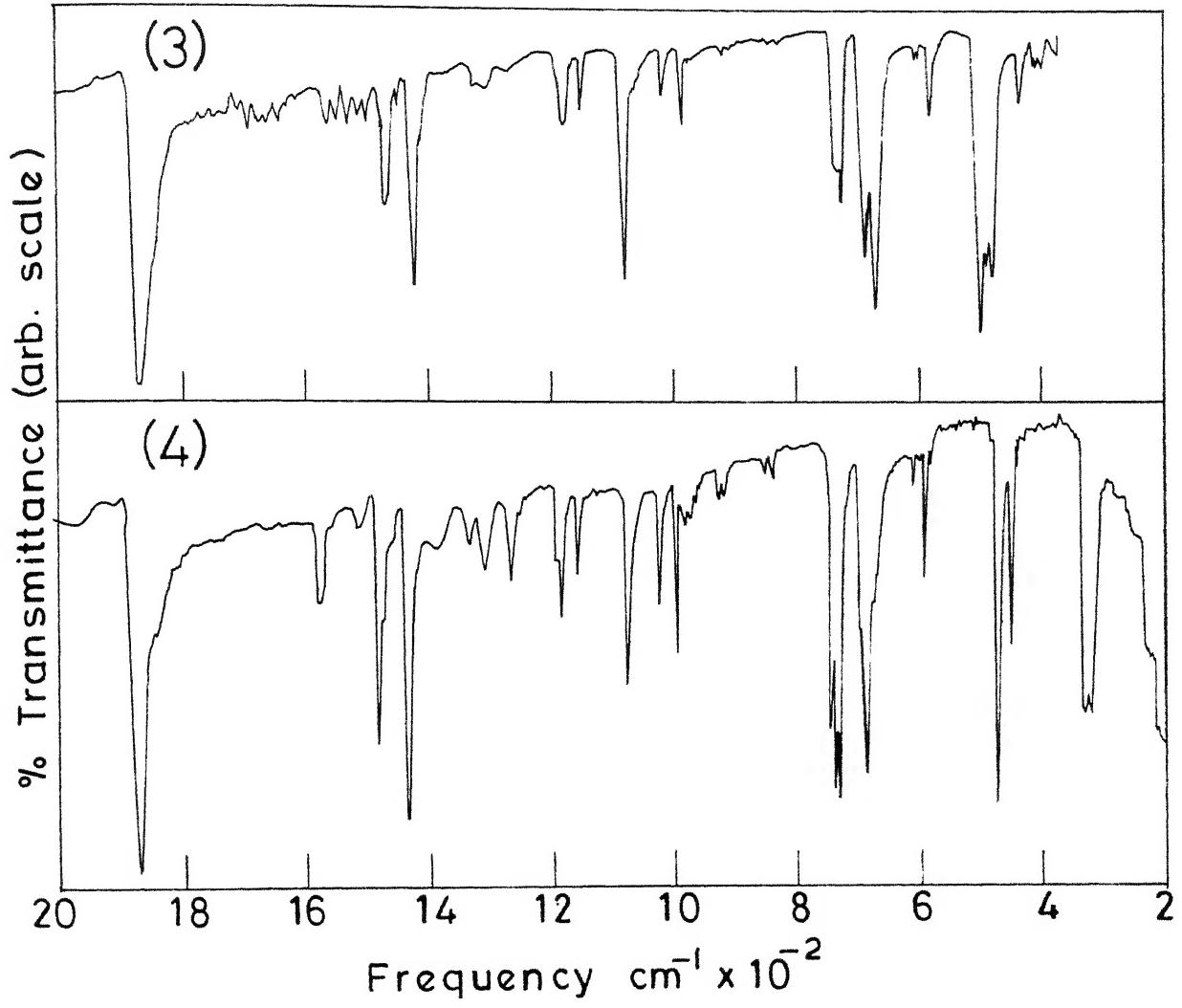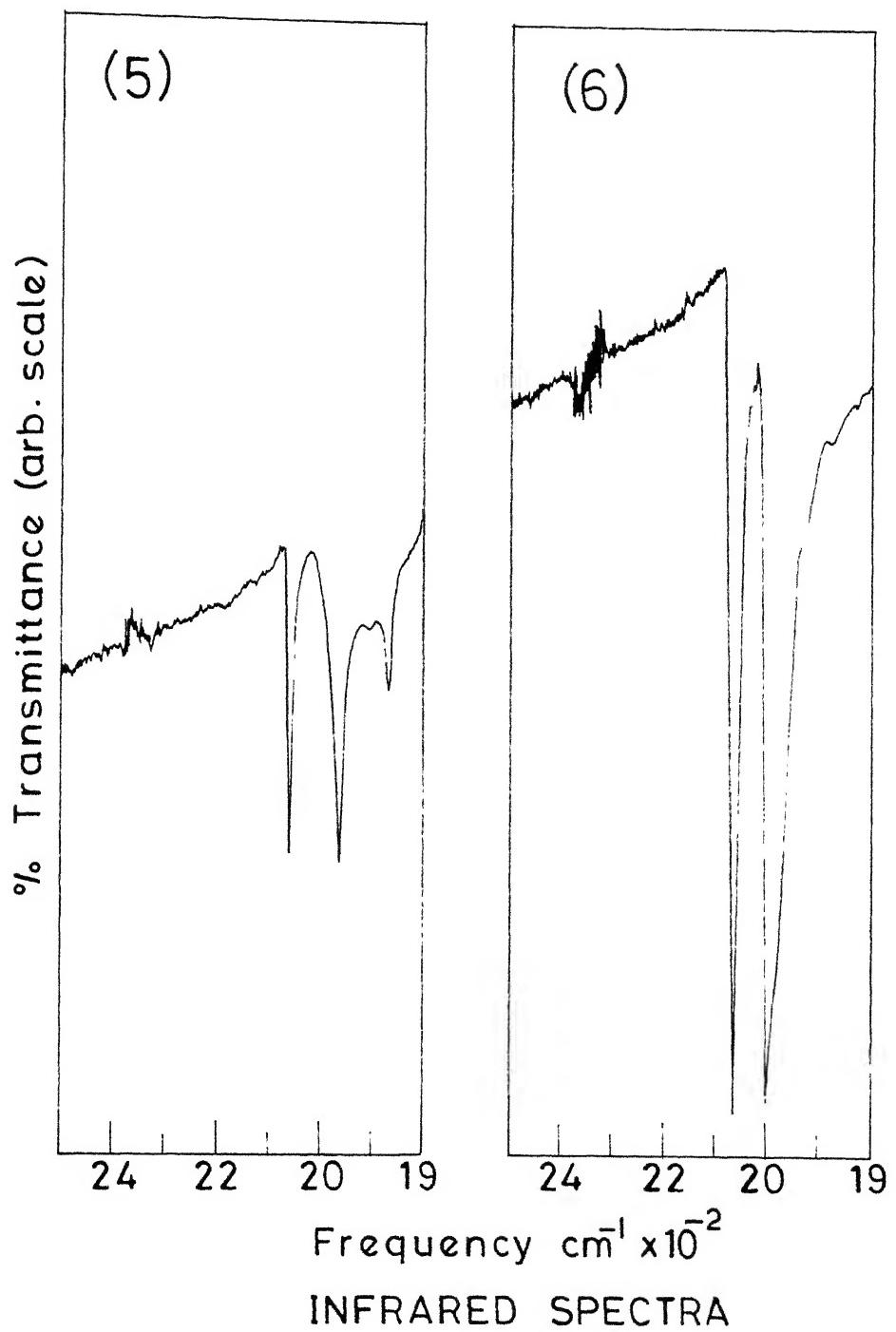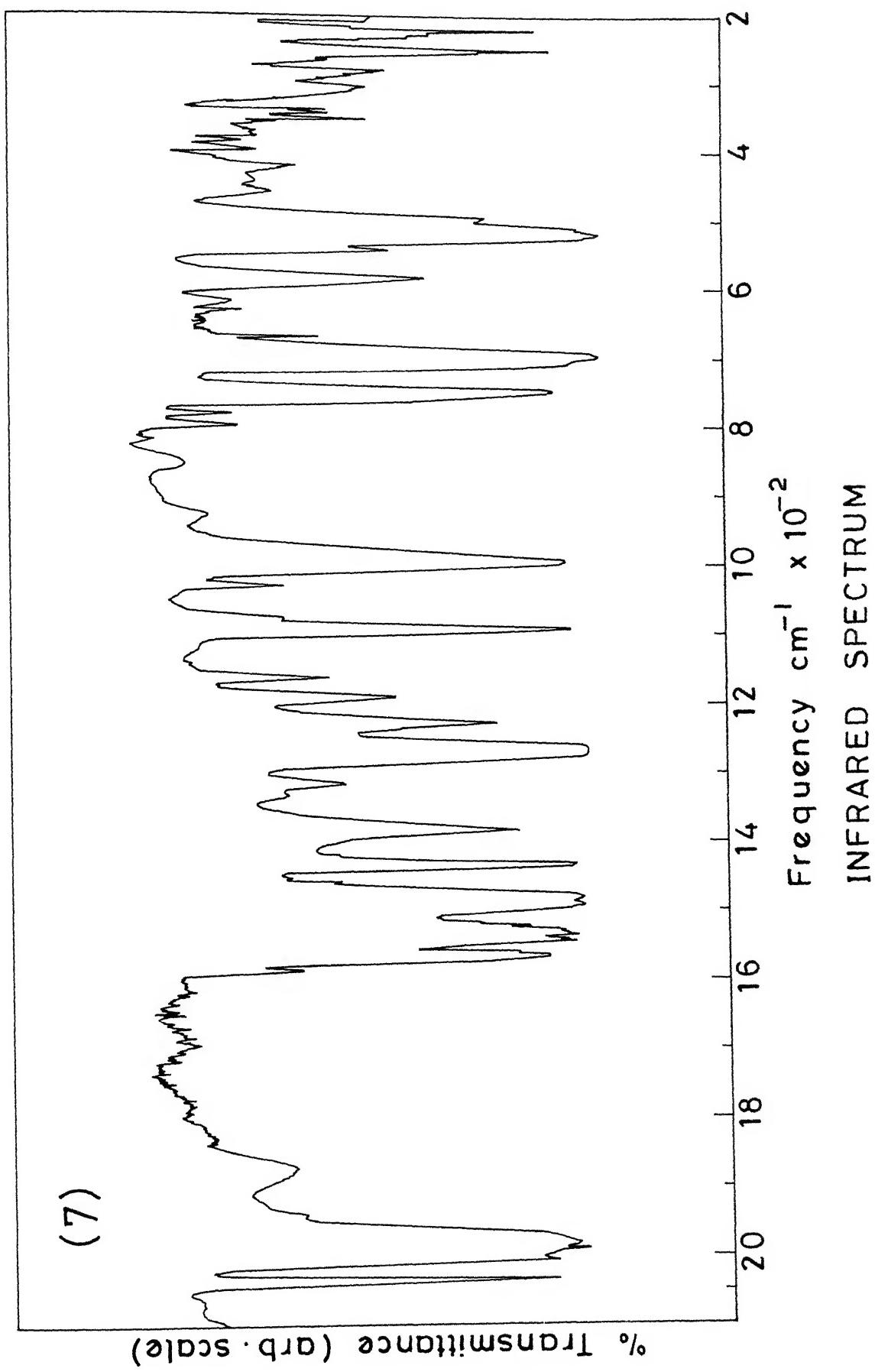
REFERENCES

1. F. Bottomley, Coord. Chem. Rev., 26, 7 (1978).

2. B.F.G. Johnson and J.A. McCleverty, Progr. Inorg. Chem., 7, 277 (1966).

3. N.G. Connelly, Inorg. Chim. Acta Rev., 6, 48 (1972).

4. J.A. McGinnety, M.T.P. Int. Rev. Sci. Inorg. Chem., Ser. One, 5, 229 (1972).

5. K.G. Caulton, Coord. Chem. Rev., 14, 317 (1975).

6. W.P. Griffith, Advan. Organomet. Chem., 7, 211 (1968).

7. F. Bottomley, Accounts Chem. Res., 11, 158 (1978).

8. R. Eisenberg and C.D. Meyer, Accounts Chem. Res., 8, 26 (1975); K.K. Pandey, S. Datta and U.C. Agarwala, Trans. Metal Chem., 4(6), 237 (1979); K.K. Pandey and U.C. Agarwala, J. Inorg. Nucl. Chem., 42, 293 (1980); K.K. Pandey, R.D. Tiwari and U.C. Agarwala, Ind. J. Chem., 20A, 370 (1981).

9. W.P. Griffith, J. Lewis and G. Wilkinson, J. Chem. Soc., 775 (1961).

10. W.L. Waters and P.J. Marsh, J. Org. Chem., 40, 3344 (1975).

11. P. Legzding and J.T. Malito, Inorg. Chem., 14, 1875 (1975).

12. N.G. Connelly and C. Gardner, J. Chem. Soc. Dalton Trans., 16, 1525 (1976).

13. K.K. Pandey and U.C. Agarwala, Z. Anorg. Allgem. Chem., 457, 235 (1979).

14. K.C. Jain, K.K. Pandey and U.C. Agarwala, Z. Anorg. Allgem. Chem., 472, 217 (1981).

15. K.C. Jain, K.K. Pandey, R. Parashad, T. Singh and U.C. Agarwala, Ind. J. Chem., 19A, 1089 (1980).

16. K.K. Pandey and U.C. Agarwala, Synth. React. Inorg. and Metal Org. Chem., 11, 25 (1981).

17. Shell Internat. Research Maatschappij, N.U. Neth. Appl. 6151 2661(C1.C015), 31, 3 (1967).

18. W.G. Burn and H.J. Bernsterin, J. Chem. Phys., 18, 1669 (1950).

19. R.L. Datta and N.R. Chatterjee, J. Am. Chem. Soc., 45, 481 (1923).

20. G. Brauer, Handbook of Preparative Inorganic Chemistry, (Academic Press, N.Y.), 1,488 (1963).

21. P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., 12, 237 (1970).

22. N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorg. Synth., 15, 50 (1974).

23. K. Natarajan, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India (1976).

24. R. Hoffman, M.M.L. Chen and D.L. Thorn, Inorg. Chem., 16, 503 (1977).

25. S.F.A. Kettle, Inorg. Chem., 4, 1661 (1965).

26. M.B. Fairy and R.J. Irving, J. Chem. Soc. A, 475 (1966).

27. J. Chatt and B.L. Shaw, J. Chem. Soc. A, 1811 (1966).

28. S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton Trans.,1 (1972).

29. B.L. Haymore and J.A. Ibers, Inorg. Chem., 14, 3060 (1975).

30. J.E. Fergusson and C.T. Page, Aust. J. Chem., 29, 2159 (1976).

31. R.E. Townsend and K.J. Coskran, Inorg. Chem., 10, 1661 (1971).

32. T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 28, 945 (1966).

33. Peter John, Chem. Ber., <u>103</u>, 2178 (1970).

34. Walter, Hieber and Peter John, Chem. Ber., <u>103</u>, 2161 (1970).

35. B.R. James and L.D. Markham, Inorg. Nucl. Chem. Lett., <u>7</u>, 373 (1971).

36. J.D. Cotton, M.I. Bruce and F.G.A. Stone, J. Chem. Soc., 2162 (1968).

37. P.C. Jain and E.C. Lingafflter, J. Am. Chem. Soc., <u>89</u>, 6137 (1967).

38. G.D. Andreetti, P.C. Jain and E.C. Lingafflter, J. Am. Chem. Soc., <u>91</u>, 4112 (1969).

39. S. Baggio and L.N. Becka, Actacryst., <u>B25</u>, 946 (1969).

INTERACTION OF NOX (X = Cl, Br or Br$_3$) AND DINITROGENTRIOXIDE WITH [Pd(PPh$_3$)$_4$], [Pt(PPh$_3$)$_4$] AND WITH PdCl$_2$, H$_2$PtCl$_6$ IN PRESENCE OF TRI- PHENYLPHOSPHINE & TRIPHENYLARSINE

During the past thirty years, a great deal of work related to the nature of bonding in nitro, nitrato and nitro- nitrato complexes has been carried out;[1] but the literature is almost devoid of the chemistry of such transition metal complex- es with tertiary-phosphine, arsine and stibines except a few reports which have appeared recently, regarding the syntheses of transition metal nitro and nitrato complexes by using nitric acid, silver nitrate, nitrogen dioxide/dinitrogen tetraoxide, dinitrogen trioxide, isoamyl nitrite, etc.[1-8] Palladium(II) nitrato complexes in presence of triphenylphosphine have been shown to catalyse the reaction of a Schiff base with 1,3-buta- diene to yield a vinylsubstituted piperidine.[9,10] It has further been observed that the dinitrogen trioxide reacted with transition metal halides and triphenylphosphine or triphenyl-

arsine to form nitrosyl and with transition metal complexes, nitrosyl-nitro or nitrato complexes.[5,7,8] Because of the varied interest in the nitro-nitrato complexes containing phosphine or arsine of transition metal ions, it will be of interest to study the reactions of N_2O_3 with some Pd(0) and Pt(0) complexes. In this chapter the results of the interactions of NOX (X = Br, Br_3 or Cl) and dinitrogentrioxide with $[Pd(PPh_3)_4]$, $[Pt(PPh_3)_4]$ and with $PdCl_2$, H_2PtCl_6 in presence of triphenylarsine and triphenylphosphine are reported.

EXPERIMENTAL SECTION

All the chemicals used were of chemically pure or Analar grade. The solvents used were doubly distilled. Wherever needed, pure and dry argon atmosphere was used.

Tetrakis(triphenylphosphine)palladium(0), tetrakis-(triphenylphosphine)platinum(0), dinitrogentrioxide, nitrosyl-chloride, nitrosylbromide and nitrosyltribromide were prepared according to the literature methods.[11-14]

(i) Reaction of dinitrogentrioxide with tetrakis(triphenyl-phosphine)platinum(0) in inert atmosphere

A solution of 0.2 g of $[Pt(PPh_3)_4]$ in 20 ml dichloromethane was treated with dinitrogentrioxide (20 ml) in deaerated CH_2Cl_2 under argon atmosphere. After the addition of N_2O_3 was complete (10 min.), the mixture was further stirred

for about 15 minutes. The reaction mixture was then concentrated under vacuum to about 2-3 ml and 10 ml of pentane was added, a white crystalline compound, $[Pt(NO_2)_2(PPh_3)_2]$ (m.p. 156°C) was separated out which was centrifuged, washed several times with deaerated pentane and dried under vacuum. It was recrystallized from CH_2Cl_2-pentane (1:3).

(ii) Reaction of dinitrogentrioxide with tetrakis(triphenyl-phosphine)palladium(0) in inert atmosphere

A solution of 0.2 g of $[Pd(PPh_3)_4]$ in 10 ml dichloromethane was treated with a saturated solution of dinitrogentrioxide in deaerated CH_2Cl_2 (20ml) under argon atmosphere. Yellow crystalline complex, $[Pd(NO_2)_2(PPh_3)_2]$ was separated out which was treated by a procedure similar to that given for $[Pt(NO_2)_2-(PPh_3)_2]$.

(iii) Reaction of dinitrogentrioxide with tetrakis(triphenyl-phosphine)platinum(0) in presence of oxygen

A solution of 0.2 g of $[Pt(PPh_3)_4]$ in 20 ml dichloromethane was purged with pure and dry oxygen for 20 minutes and the resulting solution was treated with a saturated solution of dinitrogentrioxide in CH_2Cl_2 (20 ml). After the addition of N_2O_3 was complete (10 min.), the stirring was continued for about 15 minutes. The reaction mixture was concentrated under vacuum to about 5 ml and 15 ml of dry pentane was added, whereby a white crystalline complex, $[Pt(NO_2)(NO_3)(PPh_3)_2]$ was separated out which was centrifuged, washed with hexane, and

dried under vacuum. It was recrystallized from dichloromethane-
pentane (1:3).

(iv) Reaction of dinitrogentrioxide with tetrakis(triphenyl-
phosphine)palladium(0) in presence of oxygen

A solution of 0.2 g of $[Pd(PPh_3)_4]$ in 20 ml dichloro-
methane was purged with pure and dry oxygen for 20 minutes and
the resulting greenish brown solution was treated with a satura-
ted solution of dinitrogentrioxide in dichloromethane (20 ml).
Yellow crystalline complex, $[Pd(NO_2)(NO_3)(PPh_3)_2]$ (m.p. 183°C)
was precipitated out which was purified by a procedure similar
to that given for $[Pt(NO_2)(NO_3)(PPh_3)_2)]$.

(v) Reaction of nitrosyl chloride with tetrakis(triphenylphos-
phine)palladium(0)

A saturated solution of NOCl in dichloromethane (20 ml)
was added slowly with stirring to a solution of $[Pd(PPh_3)_4]$
(0.2 g) in CH_2Cl_2 (10 ml) at room temperature. After the addi-
tion of NOCl solution was complete (5 min.), the mixture was
further stirred for about 10 minutes. The reaction mixture was
concentrated under reduced pressure and dry and deaerated
hexane was added whereupon a pale yellow coloured complex,
$[PdCl_2(PPh_3)_2]$ was precipitated out which was washed several
times with pentane and dried under vacuum.

(vi) Reaction of nitrosyl bromide with tetrakis(triphenylphos-
phine)palladium(0).

Twenty ml solution of NOBr in dichloromethane (ca. 2 M)
was added slowly with stirring to a solution of $[Pd(PPh_3)_4]$

(0.2 g) in CH_2Cl_2 (10 ml) at room temperature under argon atmosphere. After the addition of NOBr was complete, the mixture was heated under reflux for 10 minutes. A brownish orange coloured complex, $[Pd_2Br_4(PPh_3)_2]$ was separated out which was purified and dried by a procedure similar to that given for $[PdCl_2(PPh_3)_2]$.

(vii) Reaction of nitrosyl tribromide with tetrakis(triphenyl-phosphine)palladium(0)

Reaction was performed in exactly the same way as that given in section (vi) except that dichloromethane solution of $NOBr_3$ was used in place of NOBr. A brownish orange complex, $[Pd_2Br_4(PPh_3)_2]$ was obtained.

(viii) Reaction of nitrosyl chloride with H_2PtCl_6 in presence of triphenylphosphine

10 ml of an alcoholic solution of H_2PtCl_6 (0.2 g) was added with stirring to a hot ethanol solution (20 ml) of PPh_3 (1.0 g), followed by 20 ml of a saturated NOCl solution in dichloromethane. On vigorous stirring, pale yellow complex, $[PtCl_2(PPh_3)_2]$ was separated out which was centrifuged, washed with ethanol, ether and dried under vacuum.

(ix) Reaction of nitrosyl chloride with H_2PtCl_6 in presence of triphenylarsine

The reaction was performed in a similar way as that given for $[PtCl_2(PPh_3)_2]$ in (viii) except that triphenylarsine solution was added in place of triphenylphosphine. A yellow coloured

complex, $[PtCl_2(AsPh_3)_2]$ was obtained.

(x) Reaction of dinitrogentrioxide with H_2PtCl_6 in presence of triphenylphosphine

10 ml of an alcoholic solution of H_2PtCl_6 (0.2 g) was added with stirring to a hot ethanol solution (20 ml) of PPh_3 (1.0 g), followed by freshly prepared green saturated N_2O_3 solution (20 ml) in dichloromethane. On vigorous stirring, white needle shaped crystals of $[PtCl_2(PPh_3)_2]$ were obtained, which were centrifuged, washed with ethanol, ether and dried under vacuum.

(xi) Reaction of dinitrogentrioxide with H_2PtCl_6 in presence of triphenylarsine

The procedure for carrying out the reaction was similar to that given for $[PtCl_2(PPh_3)_2]$ in (x) except that a solution of triphenylarsine was added in place of triphenylphosphine. A off-white complex, $[PtCl_2(AsPh_3)_2]$ was obtained.

(xii) Reaction of nitrosyl bromide with H_2PtCl_6 in presence of triphenylphosphine

10 ml of an alcoholic solution of H_2PtCl_6 (0.2 g) was added with stirring to a hot ethanol solution (20 ml) of PPh_3 (1.0 g) followed by a freshly prepared saturated NOBr solution (20 ml) in dichloromethane. After the addition of NOBr solution stirring was continued for another 10 minutes whereby fine crystals of $[Pt(NO)ClBr_2(PPh_3)_2]$ were obtained which were

centrifuged, washed with ethanol, ether and dried under vacuum.

(xiii) Reaction of nitrosyl chloride with $PdCl_2$ in presence of triphenylphosphine

0.1 g of $PdCl_2$ was refluxed with 20 ml of a saturated solution of nitrosyl chloride in dichloromethane, followed by an addition of a hot alcoholic solution (20 ml) of PPh_3 (1.0 g). On vigorous stirring, a yellow crystalline compound, $[PdCl_2(PPh_3)_2]$ was separated out which was washed with alcohol, ether and dried under vacuum.

(xiv) Reaction of nitrosyl chloride with $PdCl_2$ in presence of triphenylarsine

Reaction was carried out by a procedure similar to that given for $[PdCl_2(PPh_3)_2]$ in xiii except that a solution of triphenyl-arsine was used in place of triphenylphosphine. A yellow crystalline compound, $[PdCl_2(AsPh_3)_2]$ was obtained.

(xv) Reaction of nitrosyl bromide with $PdCl_2$ in presence of triphenylphosphine

0.1 g of $PdCl_2$ was refluxed with (20 ml) of NOBr solution (ca. 2 M). 20 ml of a hot ethanolic solution of PPh_3 (0.5 g) was added to it. On vigorous stirring for about 20 minutes, a yellowish orange crystalline complex, $[PdBr_2(PPh_3)_2]$ was separated out which was washed with alcohol, ether and dried under vacuum.

(xvi) Reaction of nitrosyl tribromide with PdCl₂ in presence of triphenylphosphine

Reaction was performed by a procedure similar to that given in (xv) except that NOBr₃ solution (_ca._ 2 M) was used in place of NOBr. Yellowish orange crystals of [PdBr₂(PPh₃)₂] were separated out.

(xvii) Reaction of nitrosyl bromide with PdCl₂ in presence of triphenylarsine

0.1 g PdCl₂ was refluxed with 20 ml saturated solution of nitrosyl bromide and 20 ml of a hot ethanolic solution of AsPh₃ (0.7 g) was added to the solution. On vigorous stirring for 10 minutes, a yellowish orange complex, [PdBr₂(AsPh₃)₂] was separated out which was washed with alcohol, ether and dried under vacuum.

(xviii) Reaction of nitrosyl tribromide with PdCl₂ in presence of triphenylarsine

Reaction was performed by a similar procedure as that given in (xvii) except that NOBr₃ solution (_ca._ 2 M) was used in place of NOBr whereby yellowish orange complex, [PdBr₂(AsPh₃)₂] was obtained.

Carbon, hydrogen, nitrogen, phosphorus, arsenic and halogen analyses, melting points, infrared spectra and magnetic measurements were carried out according to the methods given in Chapter II. The platinum and palladium analyses were carried out by the standard methods.[15] The results are given in

Table V.1 and Table V.2.

RESULTS AND DISCUSSION

Reactions of dinitrogentrioxide with $[M(PPh_3)_4]$ (M = Pd, or Pt) in argon purged dichloromethane solution gave dinitro complexes $[M(NO_2)_2(PPh_3)_2]$ which were previously synthesized by the reactions of PPh_3 with $[M(NO_2)_4]^{2-}$.[16] Infrared spectrum of $[Pd(NO_2)_2(PPh_3)_2]$ showed characteristic bands of NO_2 at 1415, 1330 and 820 cm^{-1}. Formulation of NO_2^- ligand as N-bonded rather than O-bonded is supported by the presence of a characteristic band of N-bonded NO_2 in the region of 1320 cm^{-1}.[12-14]

Reactions of dinitrogentrioxide with $[M(PPh_3)_4]$ in presence of oxygen yielded N-bonded nitro-nitrato complexes, $[M(NO_2)(NO_3)(PPh_3)_2]$ as indicated by the characteristic bands of NO_2^- (NO_2, 1417, 1325, 820 cm^{-1}; NO_3, 1505, 1280, 980 cm^{-1}). Their formation from $[M(PPh_3)_4]$ could be explained by the following mechanism:
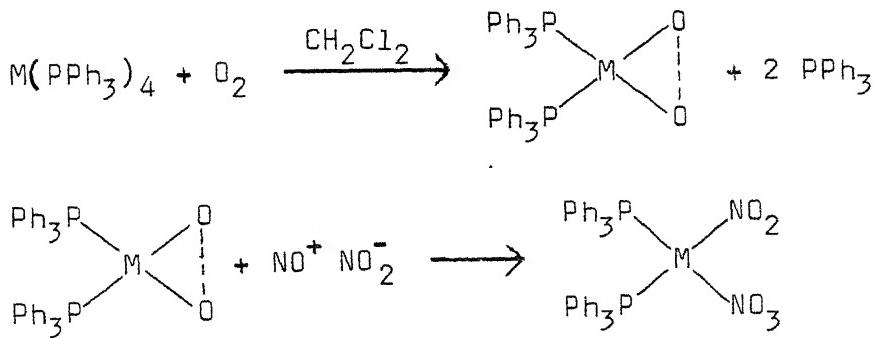
The non-conducting behaviour of these complexes in organic solvents further confirmed their nonionic nature.

The charge balance along with their diamagnetism suggested +2 oxidation state of metal ion in these complexes.

Reaction of $[Pd(PPh_3)_4]$ with nitrosylchloride gave a yellow crystalline compound, $[PdCl_2(PPh_3)_2]$ together with some triphenylphosphine oxide. Because of the ease of cis-trans isomerisation of palladium(II) complexes,[22,23] the product was always trans-$PdCl_2(PPh_3)_2$. The formation of trans-isomer was further confirmed by its melting point which coincided with the one reported earlier.[24] Both nitrosyl bromide and nitrosyl tribromide on reaction with $[Pd(PPh_3)_4]$ gave a previously reported[24] brownish orange complex, $[Pd_2Br_4(PPh_3)_2]$ (Structure I). The mechanism of the formation of
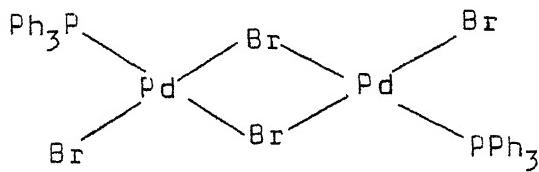
$[Pd_2Br_4(PPh_3)_2]$ can be explained by the following three steps: (a) Formation of a binary complex, $[PdBr_2(PPh_3)_2]$; (b) the reaction of the binary complex with the free bromine obtained as a result of dissociation of NOBr or NOBr$_3$ to yield an unstable species $[PdBr_4]^{2-}$; (c) the reaction of $[PdBr_4]^{2-}$ with $[PdBr_2(PPh_3)_2]$ to yield $[Pd_2Br_4(PPh_3)_2]$. This mechanism was further confirmed by the following facts: (1) Intermediate binary compound, $[PdBr_2(PPh_3)_2]$ was isolated if the same reaction was carried out at slightly lower temperature and adding relatively lesser amount of NOBr and NOBr$_3$ solutions.

(2) Chatt, et al. prepared $[Pd_2Cl_4(PPh_3)_2]$ by the interaction of $[PdCl_2(PPh_3)_2]$ with Na_2PdCl_4.[24] (3) Such a complex was not obtained by the reaction of $[Pd(PPh_3)_4]$ with NOCl which is in conformity with the stability of nitrosyl chloride at room temperature and thus non-availability of chlorine for making $[PdCl_4]^{2-}$ species.

Interactions of H_2PtCl_6 with dinitrogentrioxide in presence of triphenylphosphine or triphenylarsine gave cis-$[PtCl_2(MPh_3)_2]$ (M = P or As). Dinitrogentrioxide, PPh_3 or $AsPh_3$ in these reactions is acting as a good reducing agent, reducing platinum(IV) to platinum(II).

Reactions of NOX (X = Cl, Br, Br$_3$ or NO$_2$) with $PdCl_2$ and H_2PtCl_6 in presence of triphenylphosphine or triphenylarsine gave previously reported palladium halide and platinum halide complexes[24] respectively. Only one platinum nitrosyl halide complex, $[Pt(NO)ClBr_2(PPh_3)_2]$ was isolated by the reaction of NOBr with H_2PtCl_6 in presence of triphenylphosphine. This is in conformity with the observation that Pt(II), Pt(IV) and Pd(II) have little tendency to form nitrosyl complexes when PPh_3 or $AsPh_3$ molecules are attached to them as ligands. The i.r. spectrum of $[Pt(NO)ClBr_2(PPh_3)_2]$ showed absorption band at 1380 cm^{-1} due to ν_{NO}. The low value of ν_{NO} (1380 cm^{-1}) suggested that NO in this compound is possibly linked as a NO^- (ν_{NO}^+ for platinum and palladium metal appears in the range 1800-1825 cm^{-1} [25]). Similar reactions with $PdCl_2$

did not yield palladium nitrosyl complex. This may be largely due to higher ionization energy needed to produce Pd^{+4} than Pt^{+4} ions and it may be assumed that complexes of palladium(IV) are too unstable to be readily isolated. Dimeric nature of $[Pt(NO)ClBr_2(PPh_3)_2]$ was ruled out by the fact that the bridge in the platinic complexes is generally very weak as compared to that in platinous complexes. (Bridge of the platinic complexes readily split by oxygen containing solvents[27,28] such as ethers, alcohols, etc.)

Table V.1. Analytical data of the complexes

Complexes	ANALYSES Calculated (Found) %						
1	C 2	H 3	N 4	Cl/Br 5	P/As 6	Pd 7	Pt 8
$[Pd(NO_2)_2(PPh_3)_2]$	59.8 (59.6)	4.1 (4.0)	3.9 (3.8)	- -	8.6 (8.7)	14.7 (14.5)	- -
$[Pd(NO_2)(NO_3)(PPh_3)_2]$	58.5 (58.2)	4.0 (4.2)	3.8 (3.4)	- -	8.4 (8.2)	14.3 (14.1)	- -
$[Pt(NO_2)_2(PPh_3)_2]$	53.2 (53.0)	3.7 (3.8)	3.5 (3.6)	- -	7.6 (7.4)	- -	24.0 (23.7)
$[Pt(NO_2)(NO_3)(PPh_3)_2]$	52.2 (52.0)	3.6 (3.9)	3.4 (3.2)	- -	7.5 (7.8)	- -	23.6 (23.4)
cis-$[PtCl_2(PPh_3)_2]$	54.7 (54.6)	3.8 (3.7)	- -	8.9 (8.8)	7.8 (7.9)	- -	24.7 (24.3)
cis-$[PtCl_2(AsPh_3)_2]$	49.2 (49.3)	3.4 (3.5)	- -	8.0 (8.3)	17.0 (17.2)	- -	22.2 (22.0)
$[PdCl_2(PPh_3)_2]$	61.6 (61.6)	4.3 (4.1)	- -	10.1 (10.5)	8.8 (8.6)	15.1 (15.0)	- -
$[PdCl_2(AsPh_3)_2]$	54.7 (54.9)	3.8 (4.0)	- -	9.0 (8.7)	19.0 (19.1)	13.5 (13.2)	- -
$[Pd_2Br_4(PPh_3)_2]$	40.9 (40.7)	2.8 (2.9)	- -	30.3 (30.4)	5.9 (5.7)	20.0 (19.7)	- -

Table V.1 (contd.)

1	2	3	4	5	6	7	8
$[Pt(NO)ClBr_2(PPh_3)_2]$	45.7 (45.9)	3.2 (3.3)	1.5 (1.4)	20.7 (21.0)	6.5 (6.6)	— —	20.6 (20.3)
$[PdBr_2(PPh_3)_2]$	54.6 (54.5)	3.8 (3.8)	— —	20.2 (20.5)	7.8 (7.9)	13.5 (13.1)	— —
$[PdBr_2(AsPh_3)_2]$	49.2 (49.0)	3.4 (3.5)	— —	18.2 (17.9)	17.0 (17.2)	12.1 (12.5)	— —

Table V.2. Colour, melting point and important infrared frequencies of the complexes

Complex	Colour	M.P. (^{o}C)	Important IR Frequencies		
			ν_{NO_2} (cm^{-1})	ν_{NO_3} (cm^{-1})	Other (cm^{-1})
$[Pd(NO_2)_2(PPh_3)_2]$	Yellow	205-8	1415, 1330, 820	-	-
$[Pd(NO_2)(NO_3)(PPh_3)_2]$	Yellow	183	1417, 1325, 820	1505, 1280, 980	-
$[Pt(NO_2)(NO_3)(PPh_3)_2]$	Dull white	>250	1420, 1320, 825	1500, 1270, 1000	-
cis-$[PtCl_2(PPh_3)_2]$	White	>250	-	-	-
cis-$[PtCl_2(AsPh_3)_2]$	Off white	>250	-	-	-
$[PdCl_2(PPh_3)_2]$	Yellow	>250	-	-	-
$[PdCl_2(AsPh_3)_2]$	Yellow	>250	-	-	-
$[Pd_2Br_4(PPh_3)_2]$	Orange brown	>250	-	-	-
$[Pt(NO)ClBr_2(PPh_3)_2]$	Yellow	>250	-	-	1385
$[PdBr_2(PPh_3)_2]$	Yellowish orange	>250	-	-	-
$[PdBr_2(AsPh_3)_2]$	Yellowish orange	>250	-	-	-
$[Pt(NO_2)_2(FPh_3)_2]$	White	156-8	1420, 1320, 825	-	-

LEGEND TO THE FIGURES

Fig. V.I.   Infrared Spectra of the Complexes in KBr discs:

(1) $[Pd(NO_2)_2(PPh_3)_2]$

(2) $[Pd(NO_2)(NO_3)(PPh_3)_2]$

(3) $[PdCl_2(PPh_3)_2]$

(4) $[Pd_2Br_4(PPh_3)_2]$

(5) $[PtCl_2(AsPh_3)_2]$

(6) $[Pt(NO)ClBr_2(PPh_3)_2]$

% Transmittance (arb. scale)

Frequency, cm^{-1} x 10^{-2}

INFRARED SPECTRUM

Fig . V.I

(1)

% Transmittance (arb. scale)

Frequency, cm^{-1} x10^{-2}

INFRARED SPECTRUM

Fig. V.1

(2)

Fig. V.I

INFRARED SPECTRA

INFRARED SPECTRA
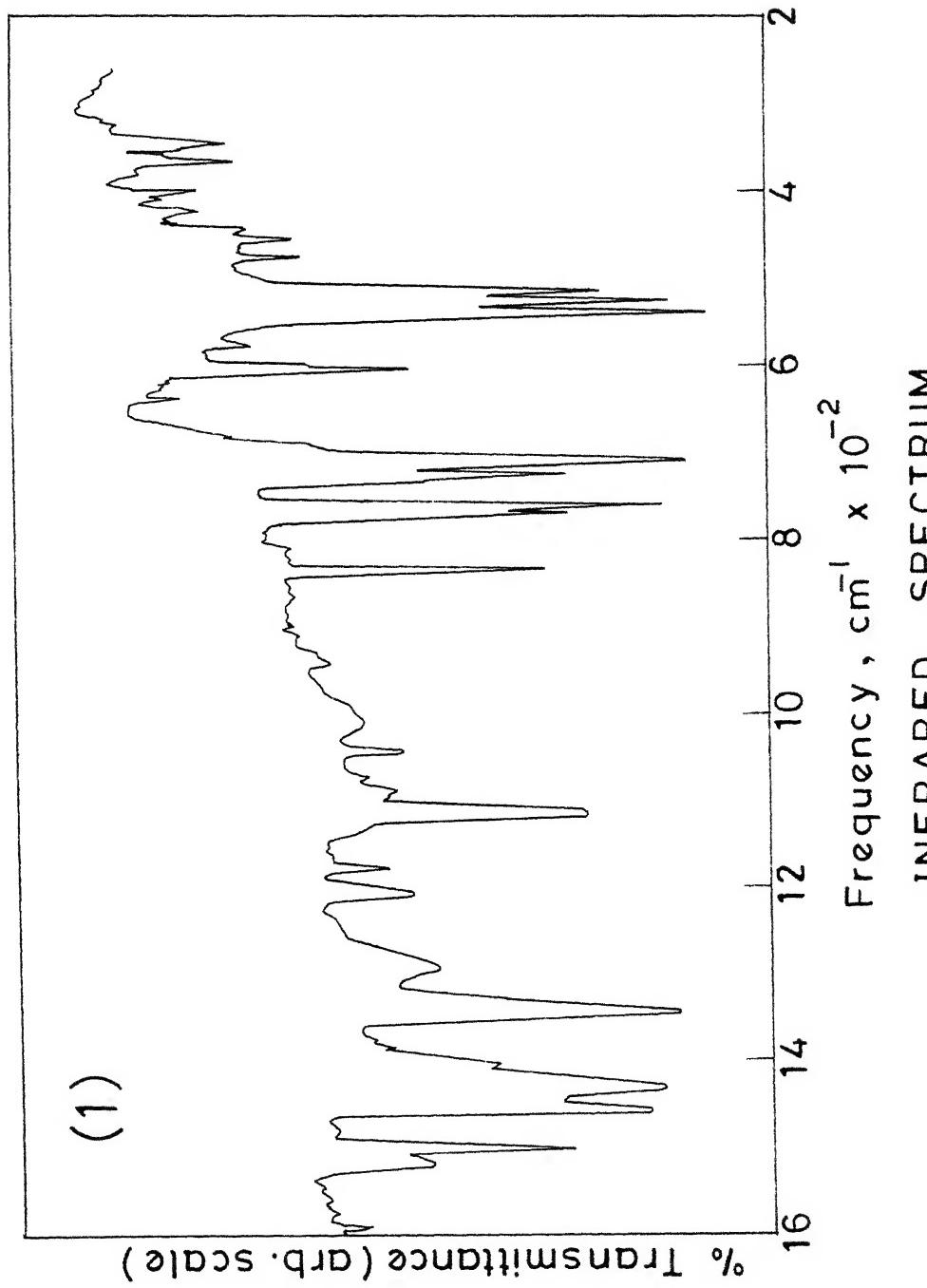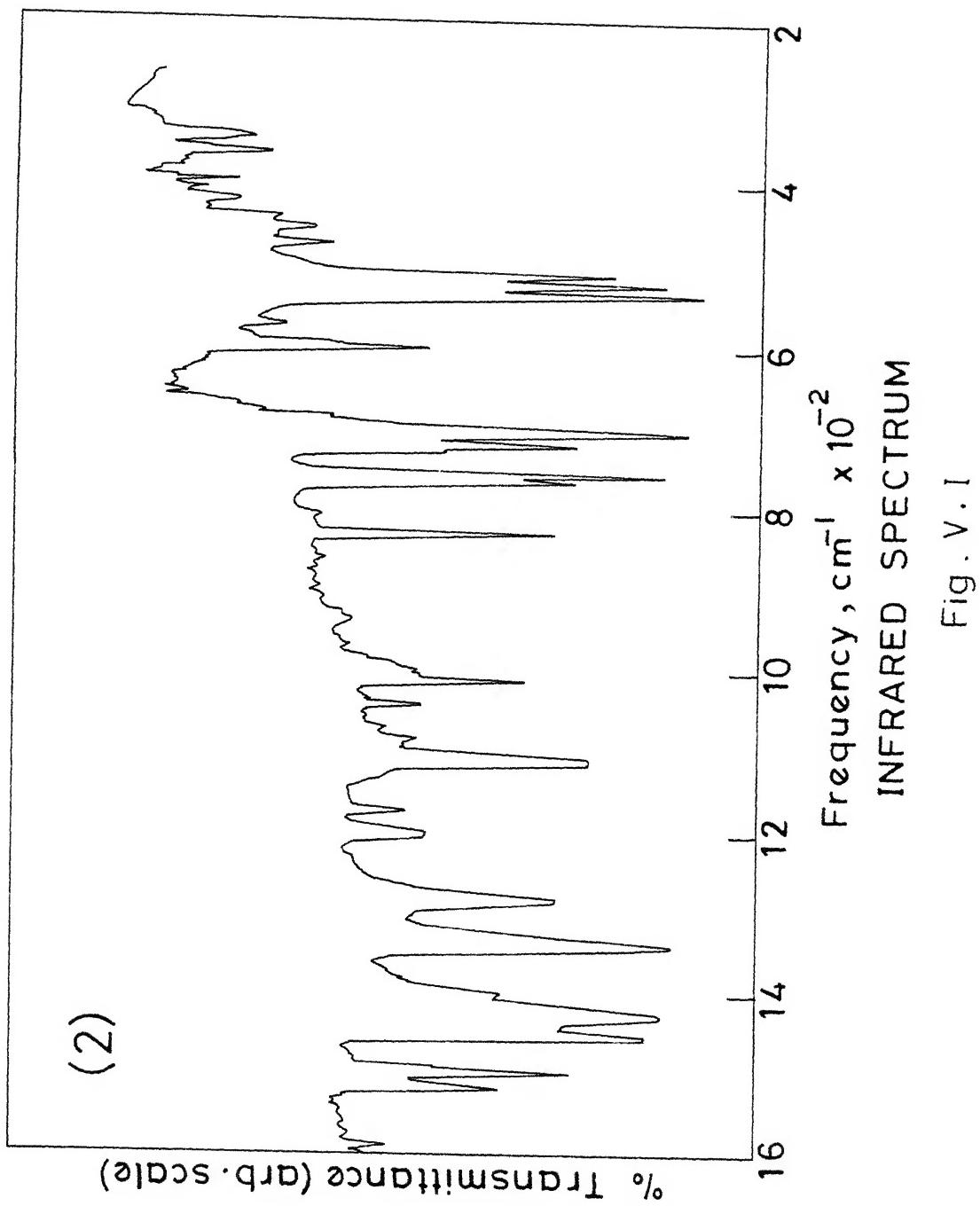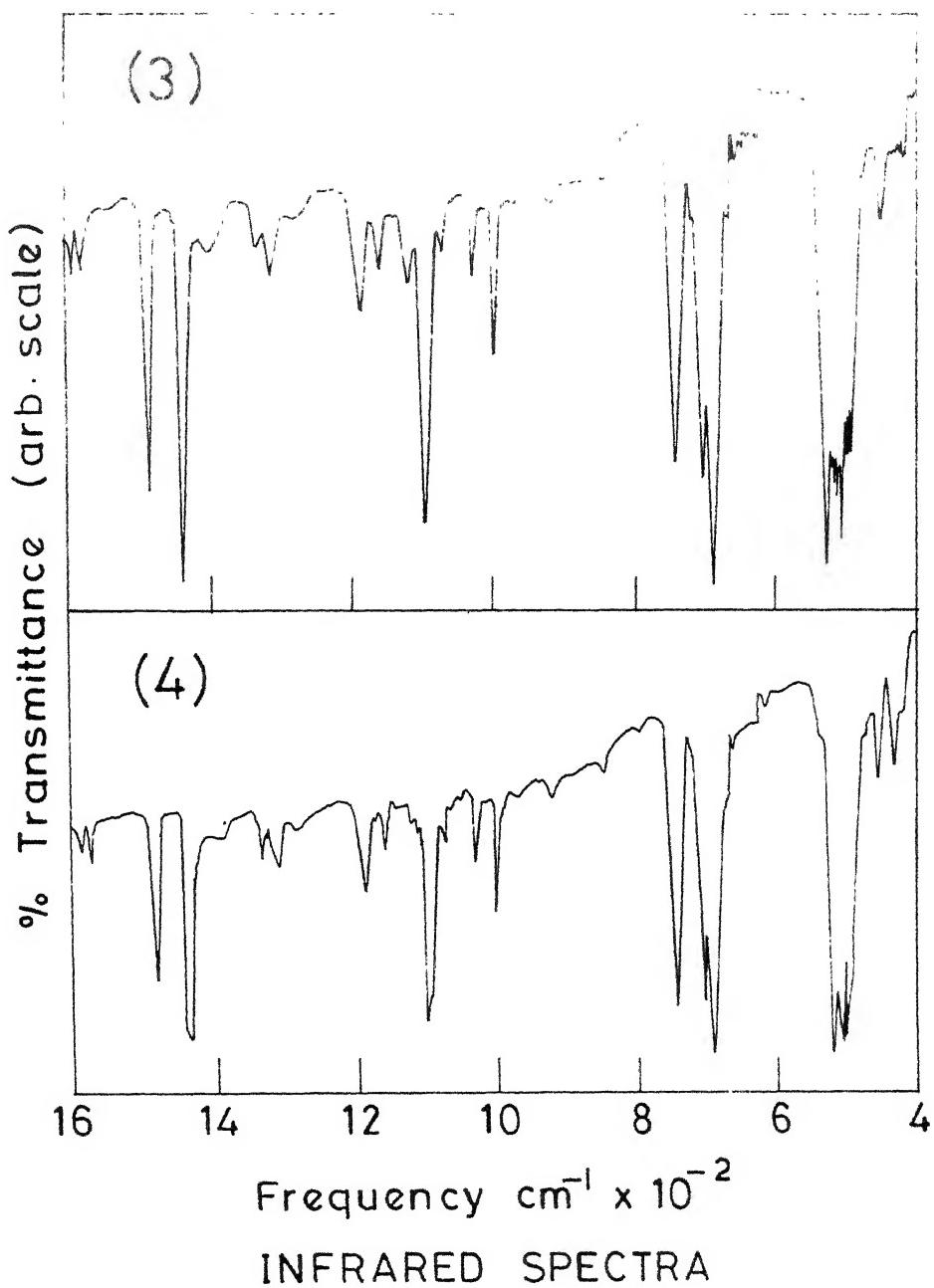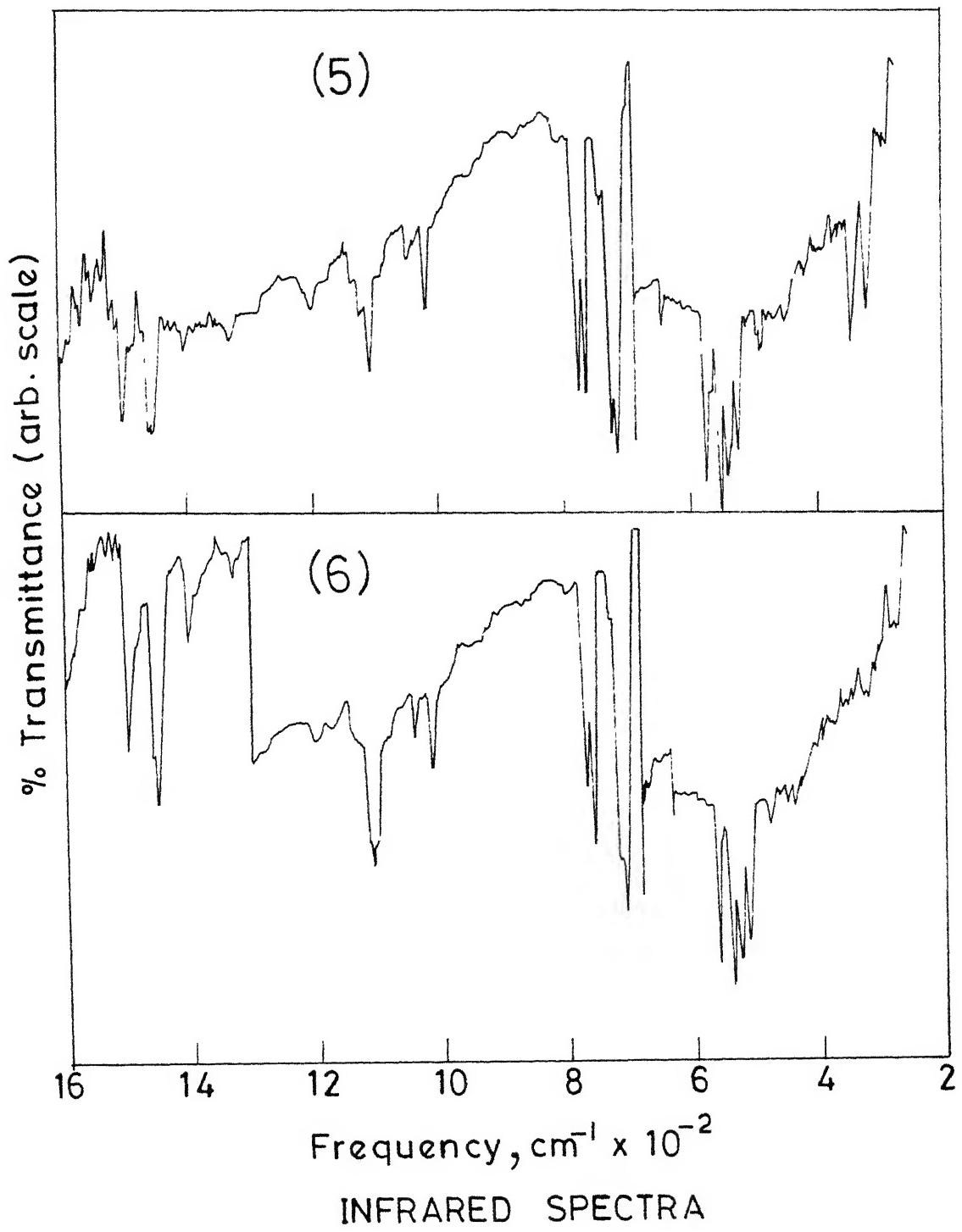
Fig V.1

REFERENCES

1. P.B. Critchlow and S.D. Robinson, Coord. Chem. Rev., 25, 69 (1978).

2. J.J. Levison and S.D. Robinson, J. Chem. Soc. (A), 762 (1971).

3. W. Beck, P. Kreutzer and Von Werner, Chem. Ber., 104, 528 (1971).

4. J.A. Kaduk and J.A. Ibers, Inorg. Chem., 16, 378 (1977).

5. K.C. Jain, K.K. Pandey, R. Parashad, T. Singh and U.C. Agarwala, Ind. J. Chem., 19A, 1089 (1980).

6. K.C. Jain, K.K. Pandey and U.C. Agarwala, Z. Anorg. Allgem. Chem., 21, 12 (1981).

7. K.K. Pandey and U.C. Agarwala, Z. Anorg. Allgem. Chem., 457, 235 (1979).

8. K.K. Pandey and U.C. Agarwala, Synth. React. Inorg. and Met. Org. Chem., 11, 25 (1981).

9. J.Furukawa, J. Kiji, H. Tomita and K. Yamamoto, Chem. Comm., 506 (1974).

10. G.D. Shier, J. Organomet. Chem., 10, P15 (1967).

11. R. Ugo, F. Cariati and G. Lamonia, Inorg. Synth., 11, 105 (1968).

12. G. Brauer, Handbook of Preparative Inorganic Chemistry, 2nd Edn., Academic Press, N.Y., 1 (1963).

13. Shell Int. Res. Maatschappij, N.U. Neth. Appl. 61 51 2661 (C1.C016), 31, 3 (1967).

14. W.G. Burn and H.J. Bernstein, J. Chem. Phys., 18, 1669 (1950); R.L. Datta and N.R. Chatterjee, J. Am. Chem. Soc., 45, 481 (1923).

15. F.E. Beamish, A textbook of Analytical Chemistry of Noble Metals,(Oxford Pergamon Press, London), 283 and 307 (1966).

16. S.L. Burmeister and R.C. Timmer, J. Inorg. Nucl. Chem., 28, 1973 (1966).

17. P.C. Jain and E.C. Lingafflter, J. Am. Chem. Soc., 89, 6137 (1967).

18. G.D. Andreetti, P.C. Jain and E.C. Lingafflter, J. Am. Chem. Soc., 91, 4112 (1969).

19. S. Baggio and L.N. Becka, Acta Crystallogr., B25, 946 (1969).

20. G. Wilke, H. Schott and P. Heimbach, Angew. Chem. Int. Edn., 6, 92 (1967).

21. C.D. Cook and G.S. Jauhol, Inorg. Nucl. Chem. Lett., 3, 31 (1967).

22. P. Fitton, M.P. Johnson and J.E. Mckeon, Chem. Comm., 6 (1968).

23. J.K. Stille, J. Am. Chem. Soc., 98, 5841 (1976).

24. F.R. Hartley, A textbook of the Chemistry of Platinum and Palladium, Applied Science Publishers Ltd., London (1973).

25. J. Chatt and L.M. Venanzi, J. Chem. Soc., 2351 (1957).

26. W.P. Griffith, J. Lewis and G. Wilkinson, J. Chem. Soc., 1775 (1959); J. Smidt and R. Jira, Chem. Ber., 93, 162 (1963).

27. J. Chatt, J. Chem. Soc., 2301 (1950).

28. R.S. Nyholm, J. Chem. Soc., 843 (1950).

CHAPTER VI

FABRICATION OF CYCLIC VOLTAMMETRIC INSTRUMENT. CYCLIC VOLTAMMETRIC STUDIES ON TRITHIAZYLTRI-CHLORIDE IN DIFFERENT APROTIC SOLVENTS AND THE EFFECTS OF ADDED TRANSITION METAL COMPLEXES

VI.1 INTRODUCTION

An increasing number of chemists use electrochemistry as a characterization technique in a fashion analogous to their use of infrared, UV·visible, NMR and ESR spectroscopy. The first step in the electrochemical characterization of a compound is to ascertain its oxidation-reduction reversibility. Cyclic voltammetry is the most convenient and reliable technique and related qualitative characterisation of a new system. The next step usually consists of the determination of electron stoichiometry of the oxidation reduction steps of the compounds. Controlled potential coulometry provides a quantitative means to such evaluations. To study the first step of electro-chemical characterization, a cyclic voltammetric instrument was fabricated by using easily available indigenous components.

A low capacity CV cell was also designed and constructed to minimise the consumption of supporting electrolytes, solvents and the electroactive species. In the second part of the chapter electrochemical behaviour of trithiazyltrichloride $(NSCl)_3$ in acetonitrile and dimethylformamide is presented. Added complexes showed a significant effect on the electrochemical behaviour of $(NSCl)_3$ in acetonitrile. Although the electrochemical processes of nitrogen oxides have been studied by a number of workers in different solvents[1-6] the studies on their thioanalogues have not yet been taken up. Recently, Tweh, et al.[7] have reported the electrochemical behaviour of S_4N_4.

Basic Principles of CV Technique

Cyclic voltammetry or cyclic triangular wave voltammetry is like polarography, a relatively simple technique, capable of providing with little experimental effort, a great deal of useful information about electrochemical behaviour. Cyclic voltammetry is itself a variant on stationary electrode voltammetry.[8] In the latter technique the potential of the stationary electrode is varied linearly, as in polarography, and the resulting current is measured on a recorder or oscilloscope. Typical stationary electrode voltammograms are illustrated in Fig. VI.1. It is clearly indicated by voltammograms that the potential may be swept either cathodically or anodically, and that unlike polarographic waves, the curves are peaked. This is a
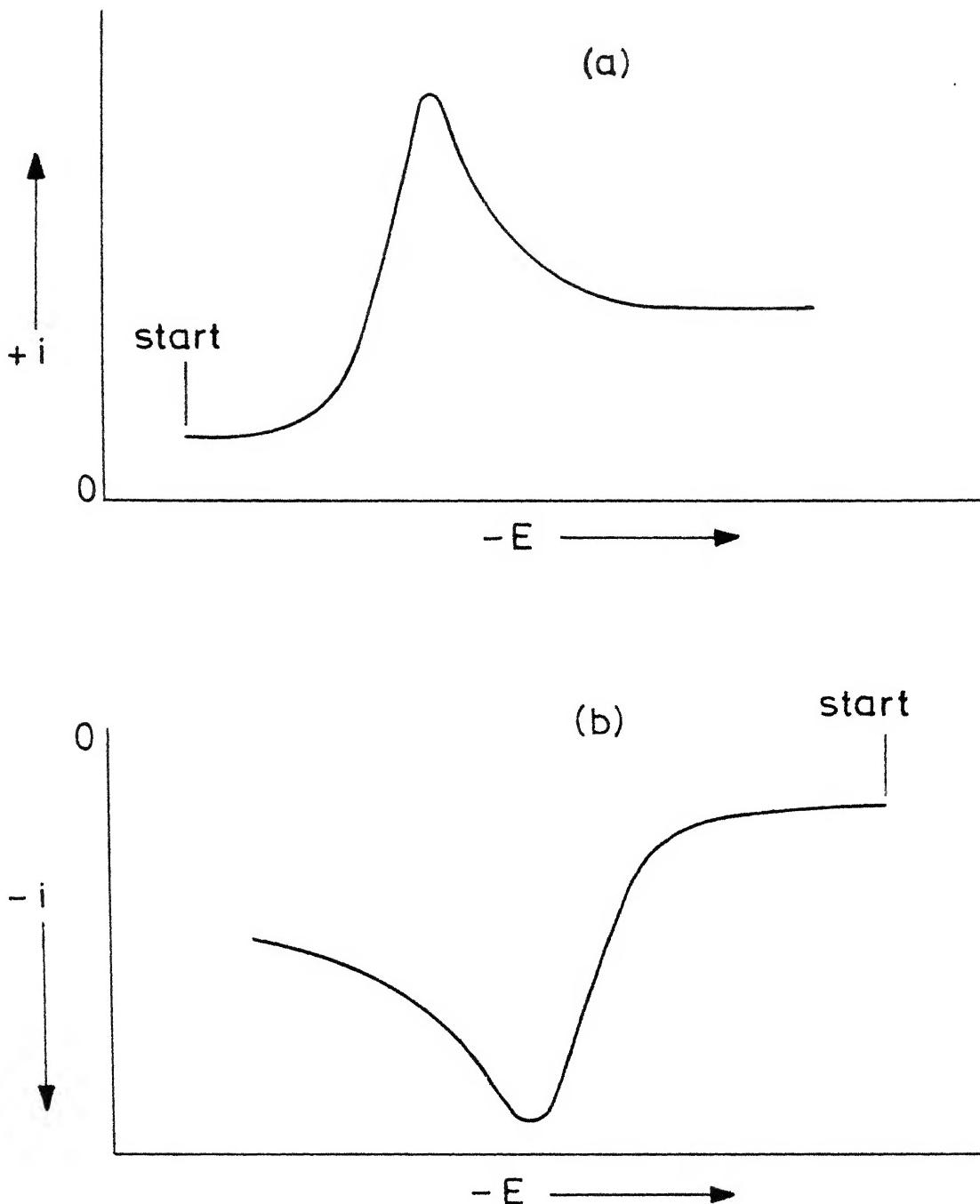
Stationary electrode voltammograms

(a) Cathodic sweep (one reduction step).

(b) Anodic sweep (one oxidation step).

Fig. VI.1

consequence of the use of a stationary electrode. As the
potential moves into the region where the substrate is reduced
(or oxidized), the region adjacent to the electrode becomes
deplected of material, and the current decreases. This peaked
behaviour is masked at a dropping mercury electrode because of
the following reasons: (1) the drop is expanding, (2) the drop
continually falls off, making fresh solution available for the
next drop, and (3) sweep rates are low in polarography. In
1948, Randles and Sevcik independently derived an equation
relating the peak current (ip) to the experimental parameters
of the stationary electrode polarographic experiment:

$$ip = 2.687 \times 10^5 \; n^{3/2} \; AD^{1/2} \; Cv^{1/2} \qquad\qquad .. \;(1)$$

where n, A, D and C are number of electron change, area of
electrode, diffusion coefficient and concentration of electro-
active species respectively. Eq. 1 predicts that the peak
current should be a function of potential sweep rate (v)(in volts
per second). Eq. 1 is based on the assumptions of a reversible
process and the linear diffusion (planar electrode). When these
conditions are fulfilled, the ratio $ip/v^{1/2}$ is found to be
constant as predicted by Eq. 1.

In CV one studies the current-potential (i-E) curve
during an electrode reaction which can be generally written as

$$ox + ne \; \rightleftharpoons \; red \qquad\qquad .. \;(2)$$
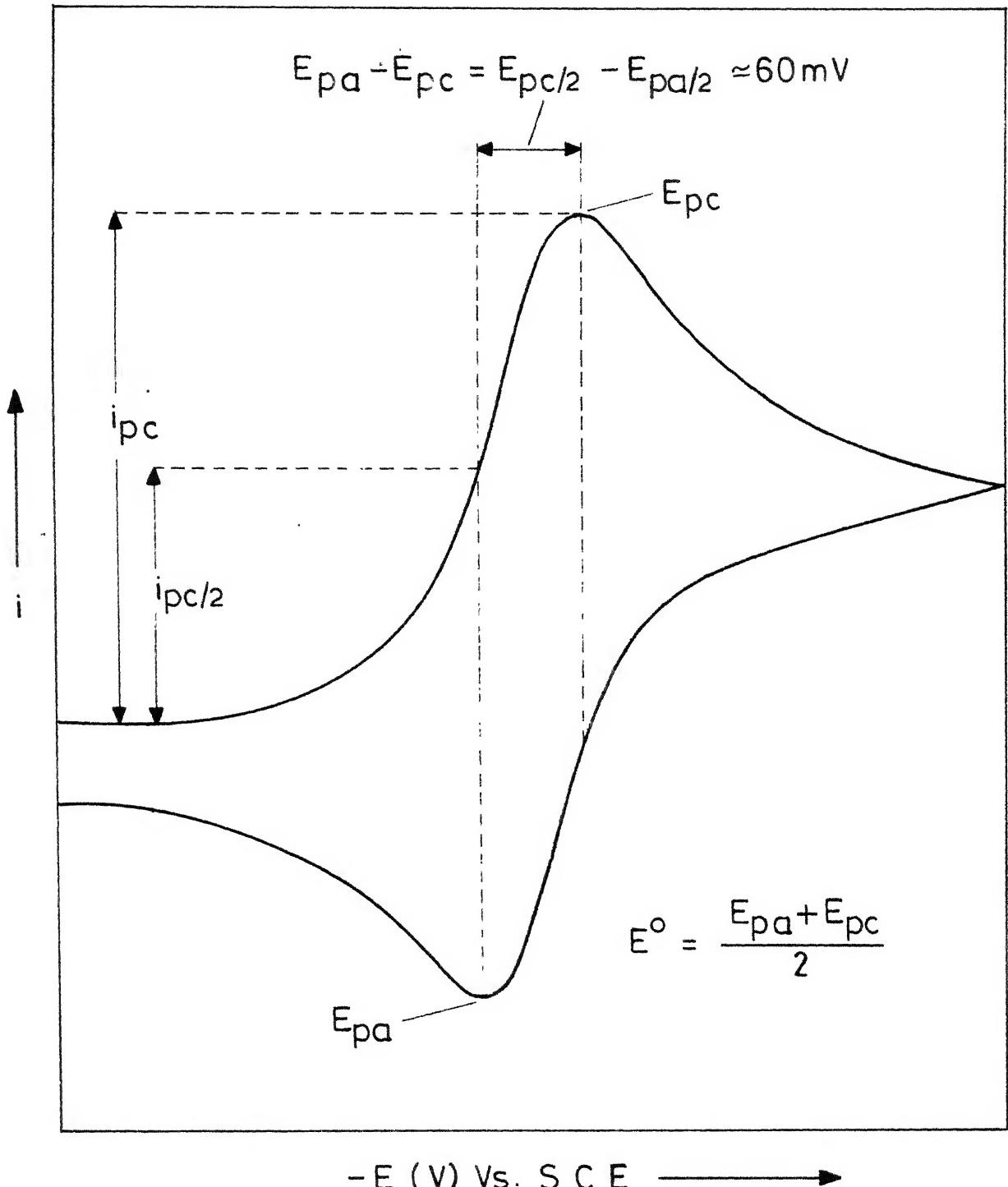
Cyclic voltammogram of a 1-electron process showing important features.

Fig. VI. 2

where ox is oxidant and red is reductant. A stationary work-
ing electrode is used and the solution is unstirred. The dc
potential (E) applied at the electrode has the isosceles tri-
angular wave form as shown in Fig. VI.3(a). The CV-gram
consists of a plot of the current flowing through the solution
as a function of potential during a cycle.

The three common types of CV-grams[10,11] are illustrated
in Fig. VI.3(c). The rate constant of the charge transfer
involved in reaction (2) is symbolised, ksh, while the poten-
tial scan rate by v. When ksh $\gg$ v, surface concentration of
electroactive species remains at or very near the Nernstian
values throughout the scan and we have reversible electron
transfer resulting in CV-gram 1 of Fig. VI.3(c). For such a
case the following relations constitute the commonly used
criterion of reversibility in CV-

$$\Delta E_p = E_{pa} - E_{pc} \approx 60/n \ mV \qquad \qquad .. (3)$$

and

$$-ip_c = ip_a \qquad \qquad .. (4)$$

where ΔE_p represents the peak-to-peak separation, ip_a and ip_c
are anodic and cathodic peak currents in microamperes and n,
the number of electrons. A typical cyclic voltammogram of one
electron process, showing important features, is shown in
Fig. VI.2.

1. Reversible
2. Quasi-reversible
3. Irreversible

(c)

(a)

(b)

Fig. VI.3   (a) Triangularwave (b) Coordinate system (c) Cyclic voltammograms
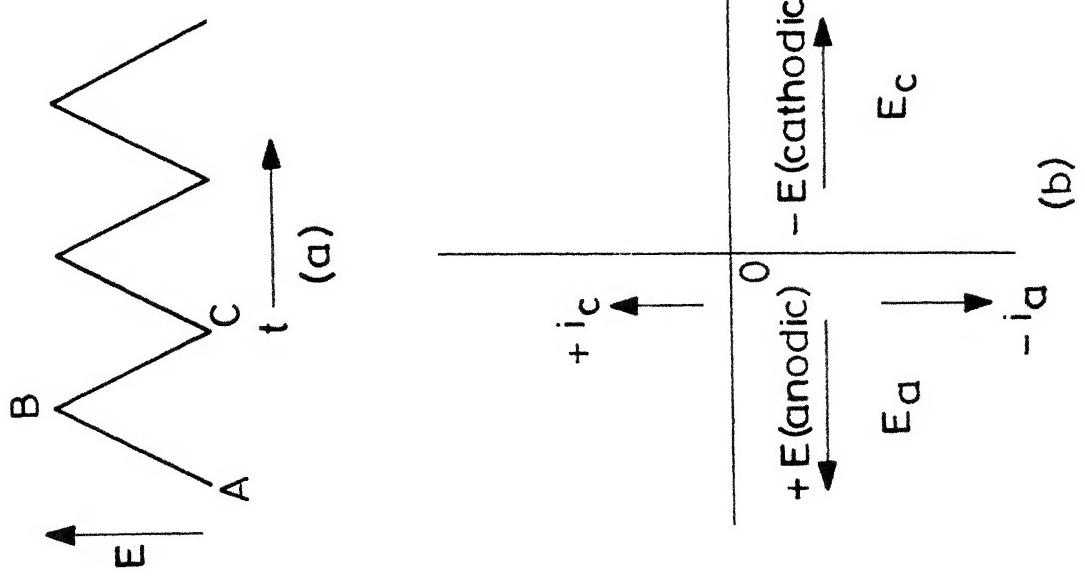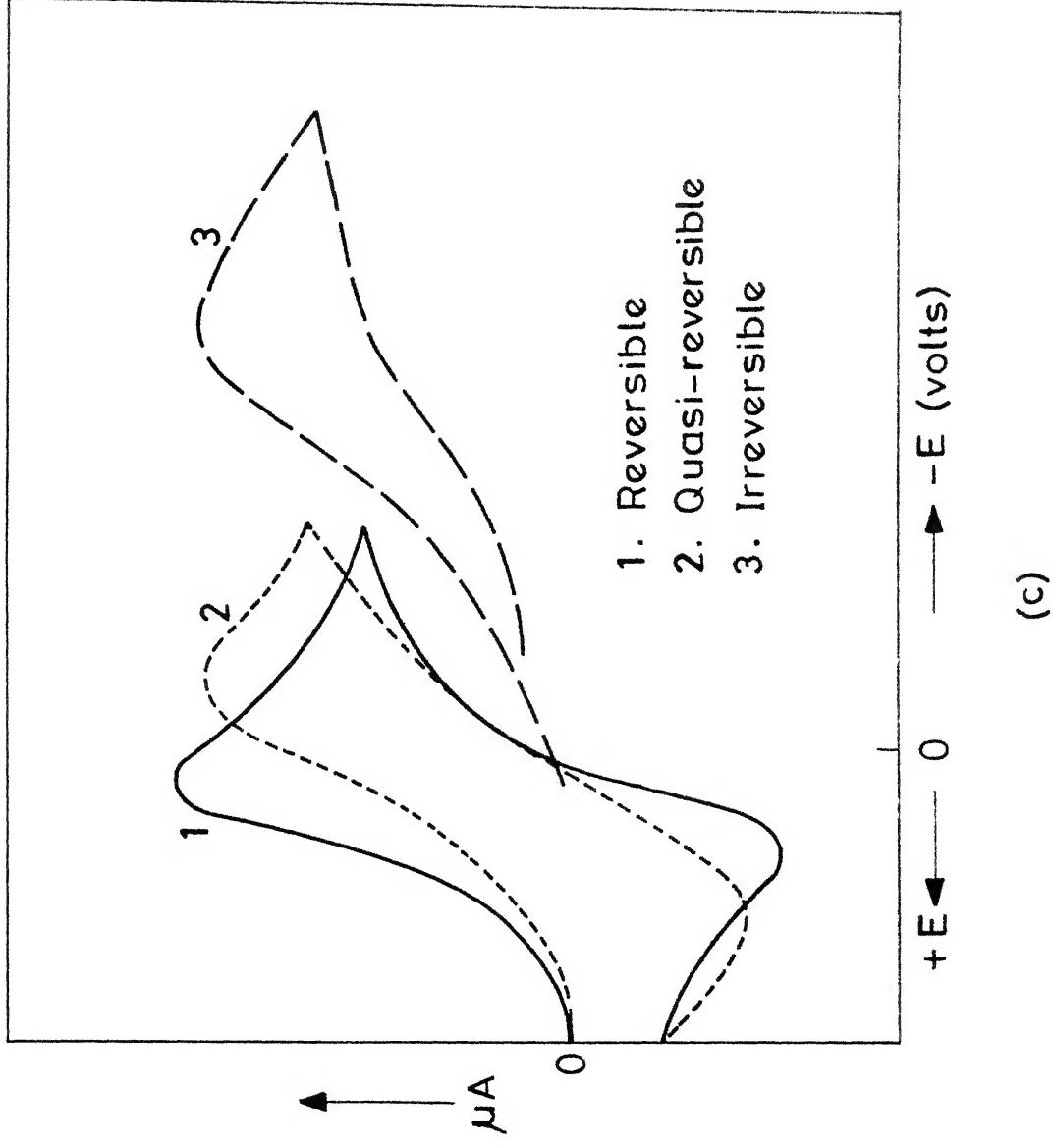
When the values of ksh and v becomes competitive, quasi-reversibility results (curve 2 of Fig. VI.3(c)), one observable effect is that both cathodic and anodic peaks get drawn out and the value of ΔE_p becomes greater than 60/n mV. Lastly when the value of ksh is smaller to that of v, E_{pc} and E_{pa} get widely separated and no current may be observed during the reverse scan as shown in curve 3 of Fig. VI.3(c). In this limit CV-gram is said to be irreversible.

The description of a system as reversible, quasireversible or irreversible is essentially operational in nature. A system may appear reversible under one set of conditions (e.g. small v) while it may appear quasi-reversible or even totally irreversible under other conditions (e.g., large v).

VI.2 EXPERIMENTAL SECTION

Cyclic Voltammetry : Instrumentation

There are four basic components of a CV instrument:

[A] Electrochemical cell and electrodes.

[B] Potentiostat.

[C] Function Generator.

[D] Recording device.

[A] Electrochemical Cell and Electrodes

In classical two electrode voltammetry, one of the electrodes used is a reference electrode (RE) and the other,

a working electrode (WE) having usually very small area. Work-
ing electrode compared to the RE is readily polarised. In
CV potential scan rate is fast and i_R drop across WE and RE is
considerable leading to the following difficulties: (i) as
current i begins to flow, the working electrode potential lags
behind the applied voltage because of the i_R drop (R being the
impedance of the cell and the electrodes) and the linearity of
the potential scan is lost. Since i_p is directly proportional to
$v^{1/2}$, it will be less than the predicted value with slower and
distorted sweep rate; (ii) current flowing through RE may cause
potential to deviate from its equilibrium (zero current) value
due to changes in concentration of the electroactive species at
the electrode surface.

To minimise such errors in voltammetric work, the three
electrode configuration (Fig. VI.4) together with an automatic
potential control device (potentiostat) has been used. The
third electrode is called counter-electrode (CE). Its volta-
mmetric characteristics are relatively unimportant. The poten-
tial controller, merely supplies whatever current is necessary
to the WE-CE circuit and the potential of the WE versus RE is
measured through a high input impedance device so that practi-
cally no current is drawn in its measurement.

Construction of Electrodes and Cell Assembly

WE used in our work is made[12] of high purity (99.9 %)
Pt-wire (0.05 cm diam.) sealed into a pyrex glass tubing as
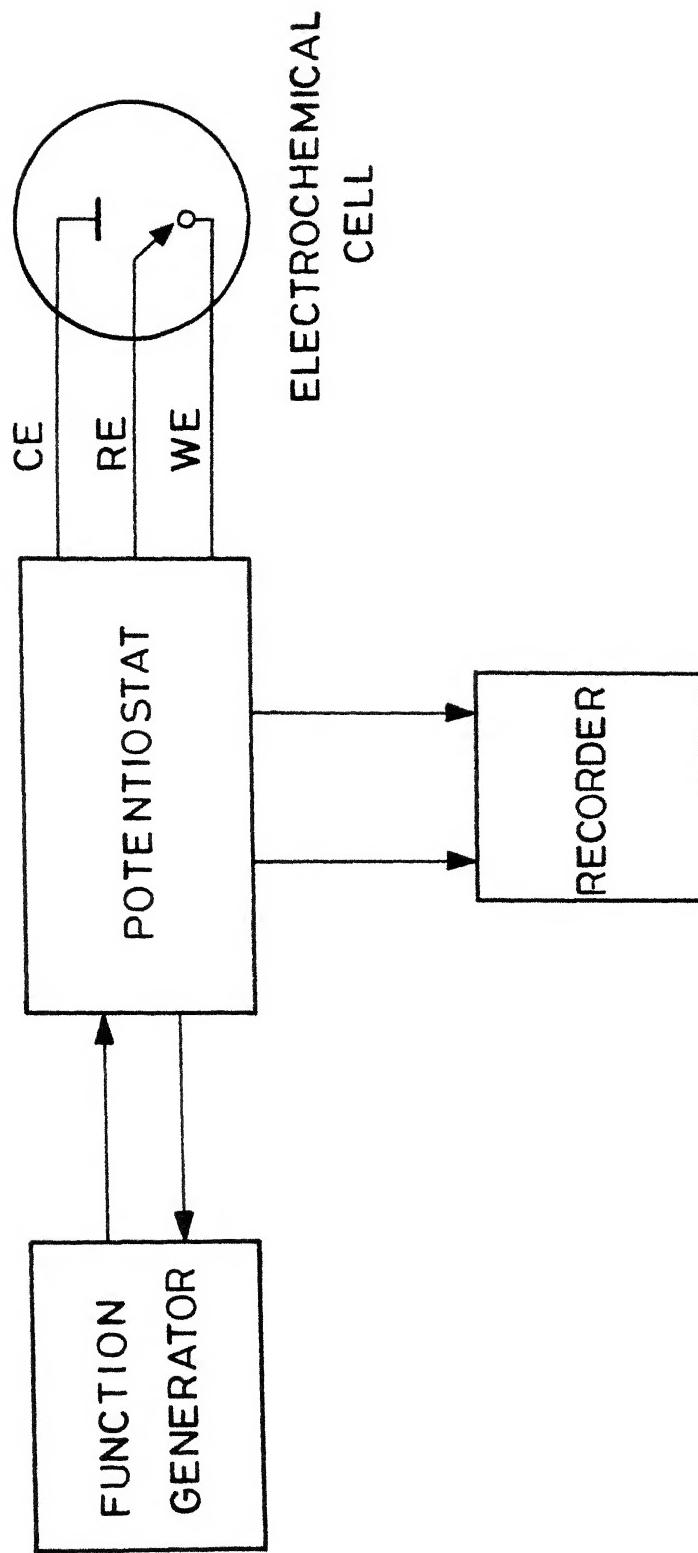
Fig. VI.4   Schematic diagram of cyclic voltammetric instrument.
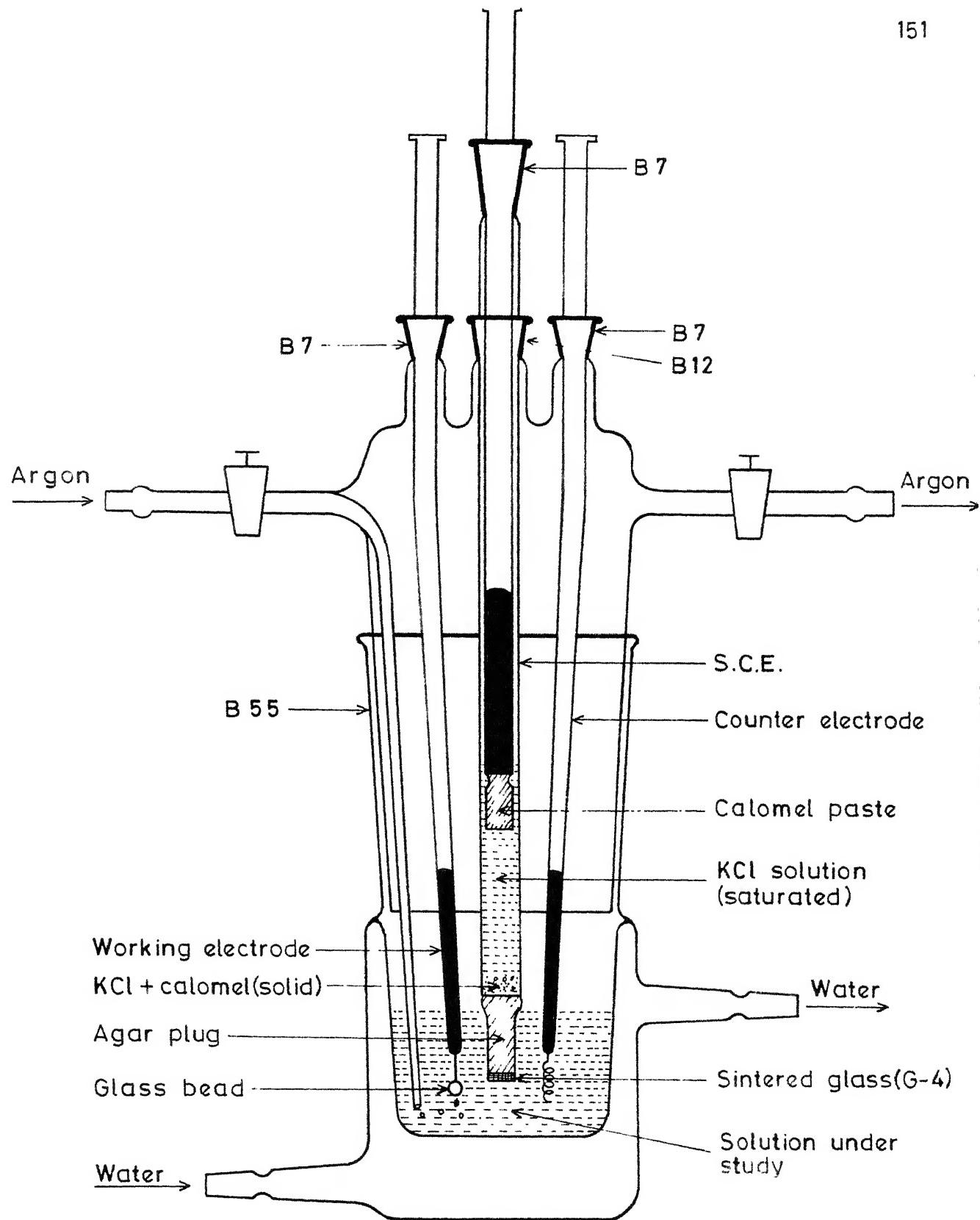
Electro chemical cell

Fig. VI.5
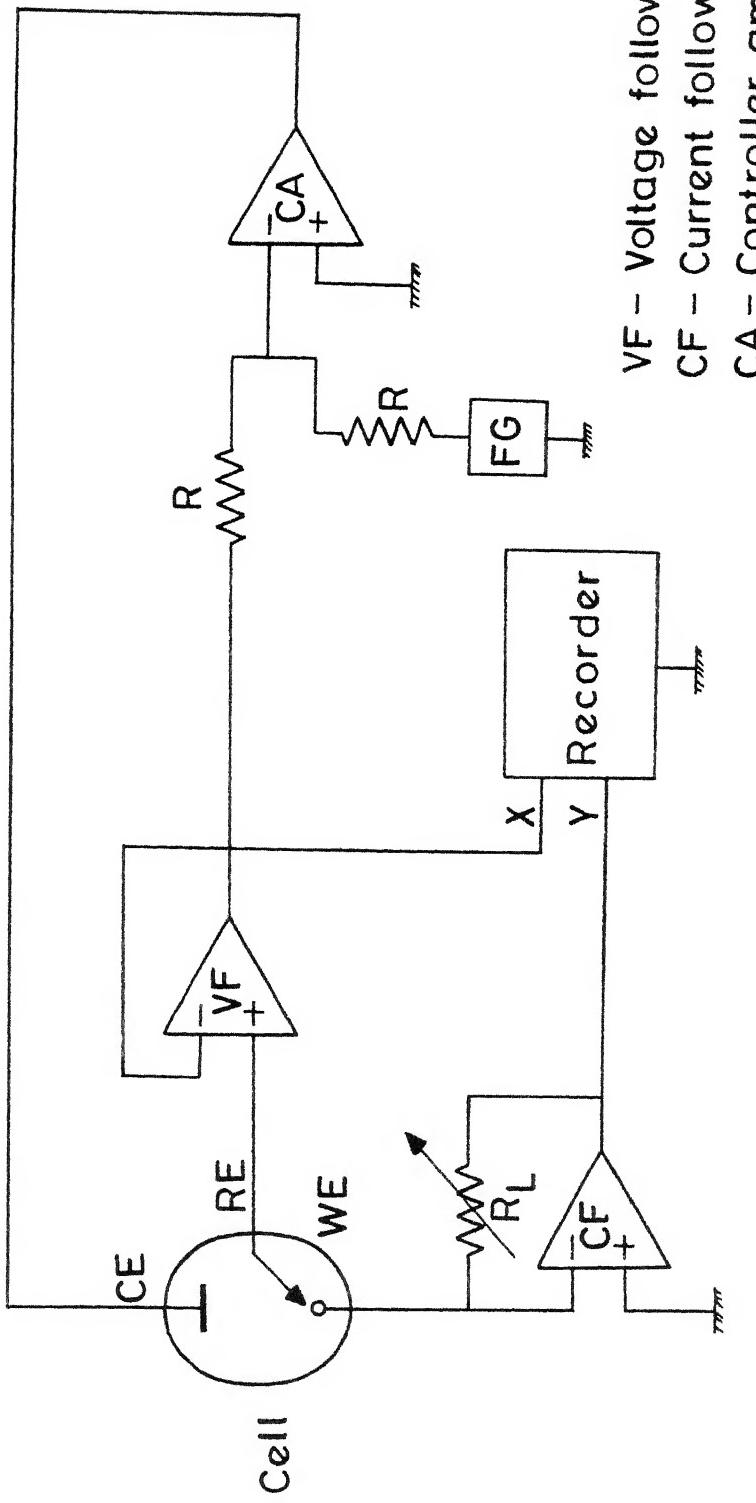
VF – Voltage follower
CF – Current follower
CA – Controller amplifier
R – Summing resistors
R_L – Current measuring resistor
FG – Function generator

Fig. VI 6   Schematic potentiostat.

seen in Fig. VI.5. The exposed end of the platinum wire is sealed into a glass bead of 1-2 mm size to eliminate end shape effect.[13,14] The counter electrode is a coiled platinum wire and the reference electrode used is a saturated calomel electrode (SCE) as shown in Fig. VI.5.[15]

Cell used is a double walled cylindrical glass vessel with an inlet and outlet tube for thermostating purpose. Inlet ending in a capilary and an outlet were provided for purging argon gas in the cap of the cell. The maximum capacity of the cell is 15 ml.

[B] Potentiostat

A potentiostat used for the first time in electro-chemistry by Hickling[14] is an automatic device that continu-ously sense the difference of potential between the working and the reference electrodes and compares the difference with a preset voltage or a time varying signal and adjust the voltage applied across the cell through a negative feedback circuit containing the CE in such a way so as to reduce the difference to zero.

The potentiostat was assembled using a solid state operational amplifier circuits, Fig. VI.6 of Spitzer[16] suitably modified by us and of Underkoffler, Shain and Mohanty.[17,18] In our system (Fig. VI.7), general purpose operational amplifiers SMC-741 and low leakage operational amplifiers NE-536 were used. In CV the double layer capacitance or charging current[19] often

154
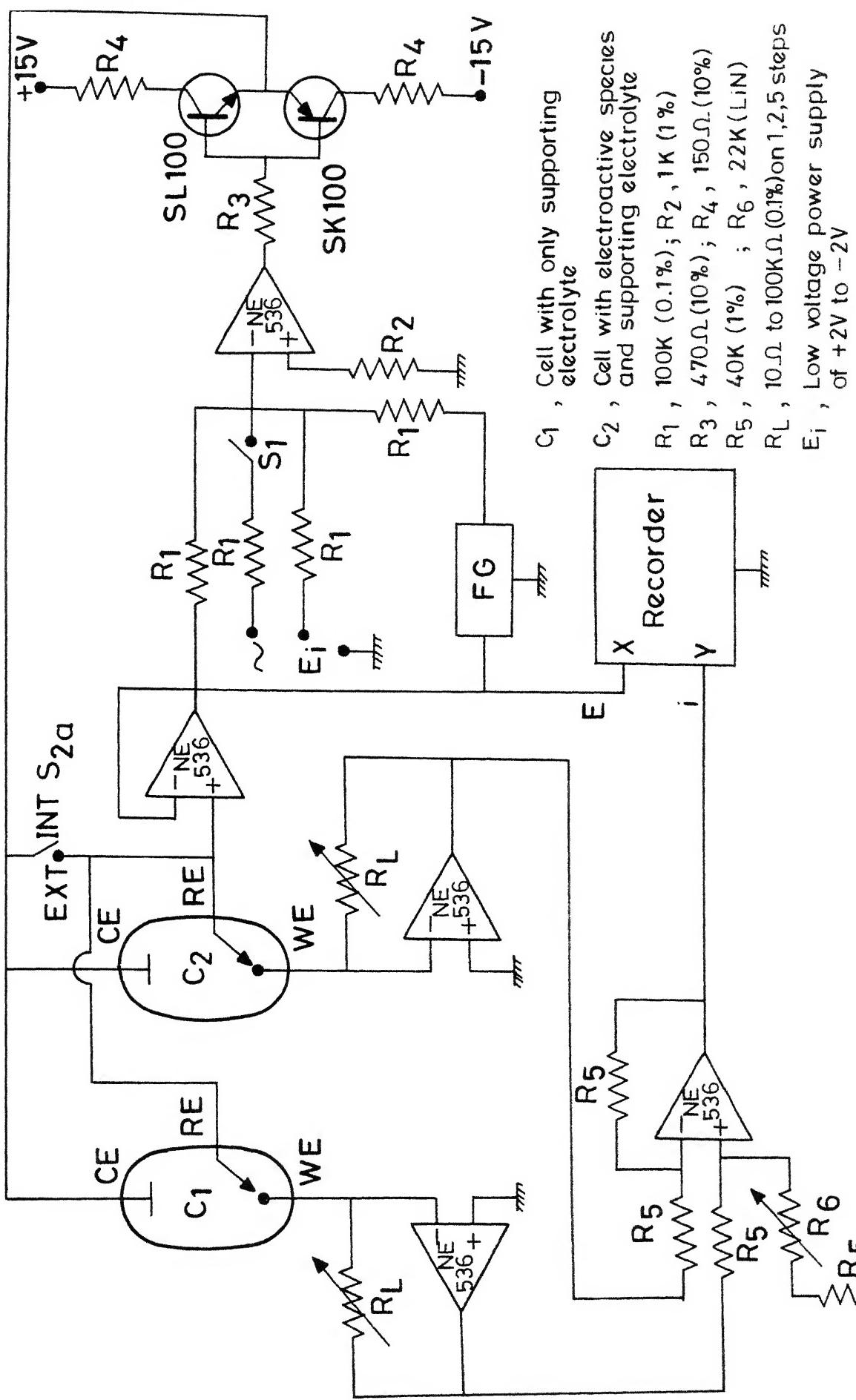
Fig.VI.7   Potentiostate circuit used by us.

C_1 , Cell with only supporting electrolyte

C_2 , Cell with electroactive species and supporting electrolyte

R_1 , 100K (0.1%) ; R_2 , 1K (1%)
R_3 , 470 Ω (10%) ; R_4 , 150 Ω (10%)
R_5 , 40K (1%) ; R_6 , 22K (LiN)
R_L , 10 Ω to 100KΩ (0.1%) on 1,2,5 steps
E_i , Low voltage power supply of +2V to −2V

contribute to a considerable extent especially when Pt electrodes are used. The order of magnitude of the double layer capacity[20] at the platinum is 20-40 $\mu F/cm^2$. To compensate the charging current we have modified the potentiostat circuit by using two three electrode cells of the same design. One of the cells (experimental cell) contained the electroactive substance in addition to supporting electrolyte, the other cell (reference cell) had only the supporting electrolyte. The same potentio-stat controlled the potential of two cells but the working electrodes were connected to separate current followers. The output of these current followers were used as inputs to a subtractor which gave the current output (contribution from only the electroactive species) to be recorded. To obtain meaningful results, following conditions are to be met:[21]

i) The concentration of the supporting electrolyte should be identical in the experimental and reference cells;

ii) The electroactive species should not significantly influence the double layer capacity;

iii) The surface characteristics of both working electrodes should be as close to each other as possible;

iv) The charging current signals generated in the experi-mental and reference cell should correspond to the same electrode area.

Condition (i) is trivial, condition (ii) in our studies is not precisely known but for the present it was assumed not

to contribute significantly and conditions (iii) and (iv) can
not be met precisely for the Pt-wire electrodes. To minimise
this difficulty, the input to the subtractor from the experi-
mental cell was fixed at unity gain whereas the input from the
reference cell is kept variable.

(c) <u>Function Generator</u>: We have fabricated the signal genera-
tor using basically the circuit of Myers and Shain[22] with some
modifications.

In the function generator the cell potential was fed back
to the signal generator to define the circuit operation in
terms of the real performance of the potential control. This
unit produced ramp and hold signals, single cycle and multi-
cycle triangular waves with independently selectable initial
potential (E_i) Fig. VI.8, anodic (E_A) and cathodic (E_C) limit
potentials and hold potential (E_H). The scan rates available
from the unit were in the range,[22] 0.2 mV/sec to 1000 V/sec.

The comparison voltage for the cathodic limit, anodic
limit and the hold potential for ramp and hold signals were set
through the low voltage power supplies, E_C, E_A and E_H respectively.
The operational amplifiers used in our circuit were NE-536 found
capable of switching rapidly from one limit to other. A quad
2-input NAND gate EC-700 was suitably connected to act as a
dual R-S flip flop. An array of six SH-100 diodes performed
as the diode gate in the ramp and hold single cycle operation.
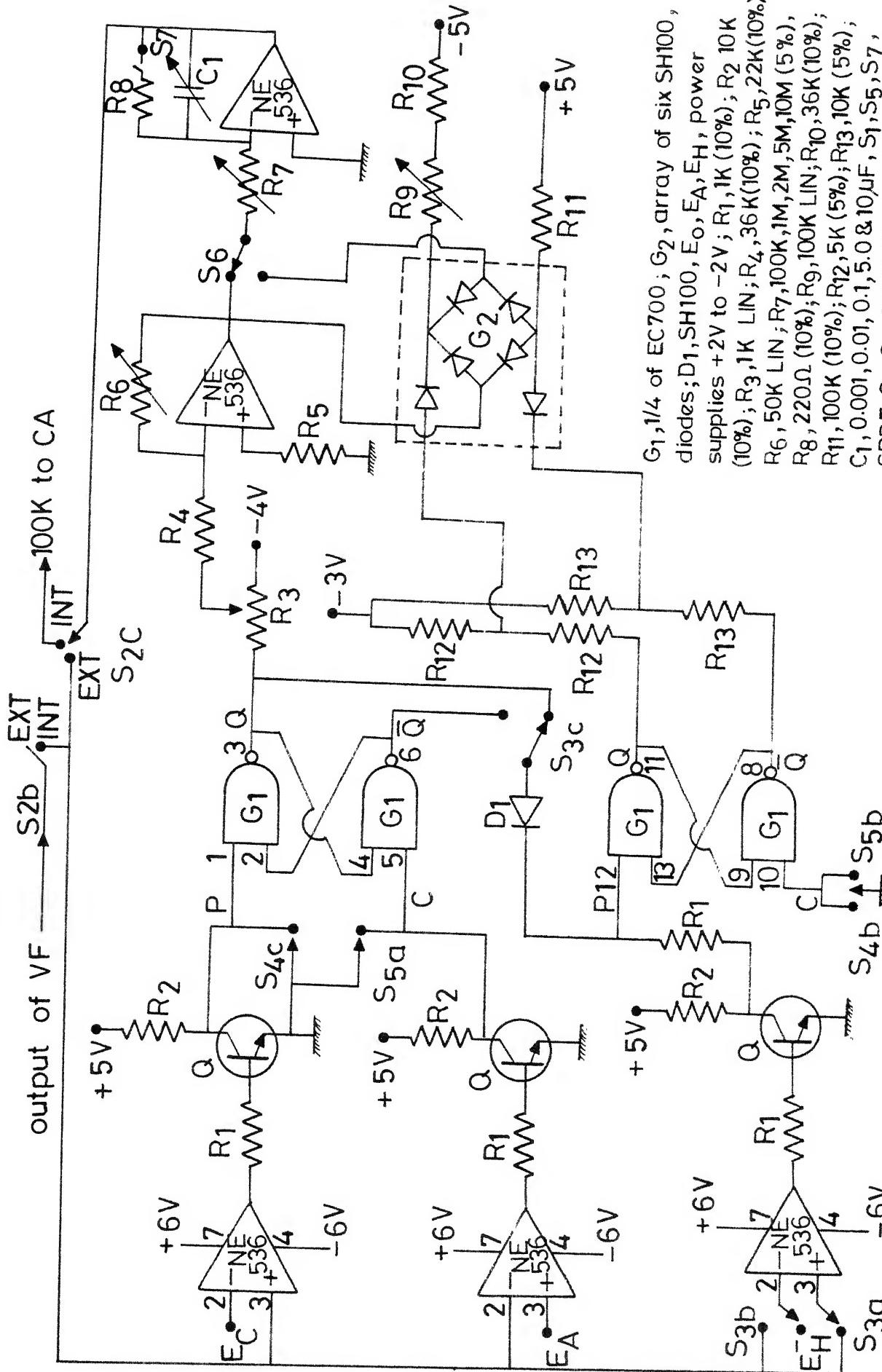
Fig. VI.8   Function generator circuit used by us.

G_1, 1/4 of EC700; G_2, array of six SH100, diodes; D_1, SH100, E_o, E_A, E_H, power supplies +2V to −2V; R_1, 1K (10%); R_2 10K (10%); R_3, 1K LIN; R_4, 36K(10%); R_5, 22K(10%) R_6, 50K LIN; R_7, 100K, 1M, 2M, 5M, 10M (5%), R_8, 220Ω (10%); R_9, 100K LIN; R_{10}, 36K (10%); R_{11}, 100K (10%); R_{13}, 10K (5%), R_{12}, 5K (5%); R_{13}, 10K (5%), C_1, 0.001, 0.01, 0.1, 5.0 & 10μF, S_1, S_5, S_7, SPDT, S_2, S_3, S_3, 3PDT, S_4, S_5, SPDT momentary contact, Q, 2N2368.

Various output wave forms available from this generator are shown in Fig. VI.9.

The required voltages for the potentiostat and the signal generator were derived by suitable circuitry from a ± 15 V stabilized power supply (Net Works, India Ltd.). The circuits used by us is shown in Fig. VI.10. The potentiostat and the signal generator were assembled in an aluminium box with control pannels as seen in the photograph (Fig. VI.11).

[D] Recording devices

The cyclic voltammograms were monitored first on an oscilloscope (ECIL model OS763A) and then recorded on a X-Y recorder (Digilog model 2000). Instrument performance was tested with the standard redox systems[23] $[K_4Fe(CN)_6]$ and $[Ru(NH_3)_5Cl]Cl_2$ as shown in Fig. VI.12(a) and VI.12(b).

Preparation of .Complexes

All the complexes, $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$, $NiCl_2(PPh_3)_2$, $RuCl_3(AsPh_3)_2 \cdot MeOH$, $Ru(CO)_3(PPh_3)_2$ and $(NSCl)_3$ were prepared according to the literature methods.[24]

Solvents and Supporting Electrolytes

Tetraethylammonium perchlorate (TEAP) was used as supporting electrolyte and purchased from Fluka AG.TEAP was dried before use under vacuum at $80^\circ C$. Acetonitrile (CH_3CN) (E. Merck, India) was triply distilled over P_4O_{10} and bubbled with dry
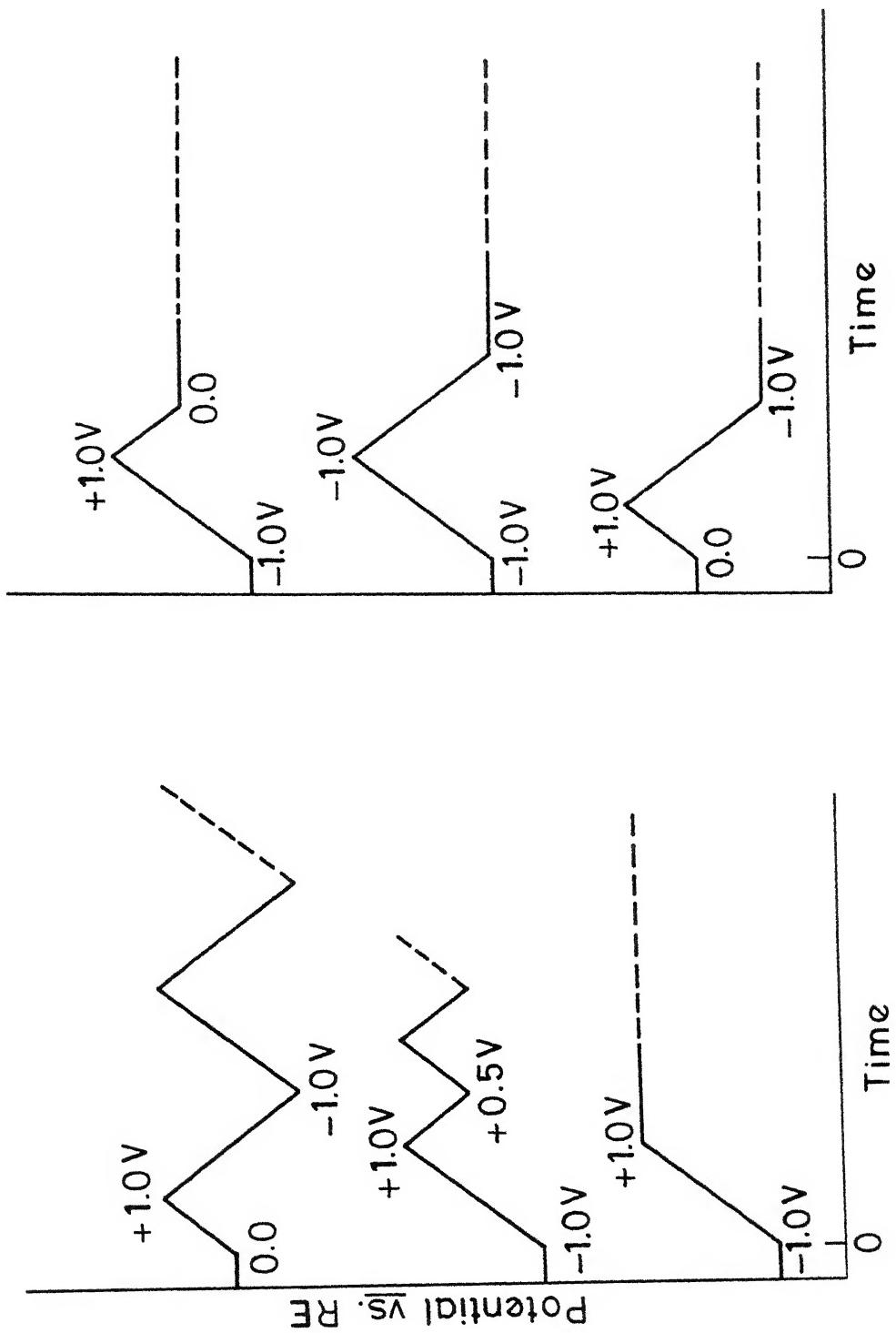
Fig. VI.9   Examples of the type of functions available from the function generator.

E_2

68Ω, 5%, 1W

Q

output

R₁
5%, 1/2W

470Ω, 1/2W

220Ω, 10%, 1/4W

1K, 5%, 1/2W

741

(a)

5K, 5%, 1/2W

1.5K, 10%, 1/2W

E₁

E_1	E_2	R_1	Q	Output
−15V	+15V	1.8K	SL100	+6.0V
+15V	−15V	1.8K	SK100	−6.0V
−15V	+15V	1.5K	SL100	+5.0V
+15V	−15V	1.5K	SK100	−5.0V
+15V	−15V	1.0K	SK100	−4.0V
+15V	−15V	820Ω	SK100	−3.0V

(a) For supply of ±6, ±5, −4 and −3 volts.

output
+2 to −2V

741

10K

−15V

1K, LIN, 1/2W

250Ω, LIN, 3W

1K, 10% 1/4W

+15V

−15V
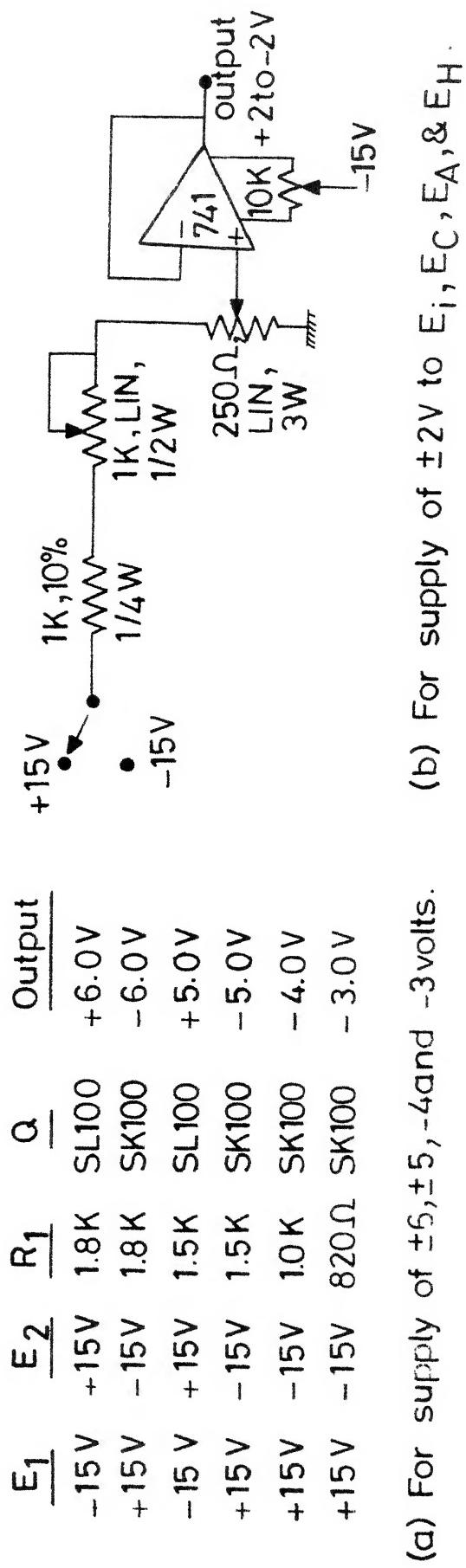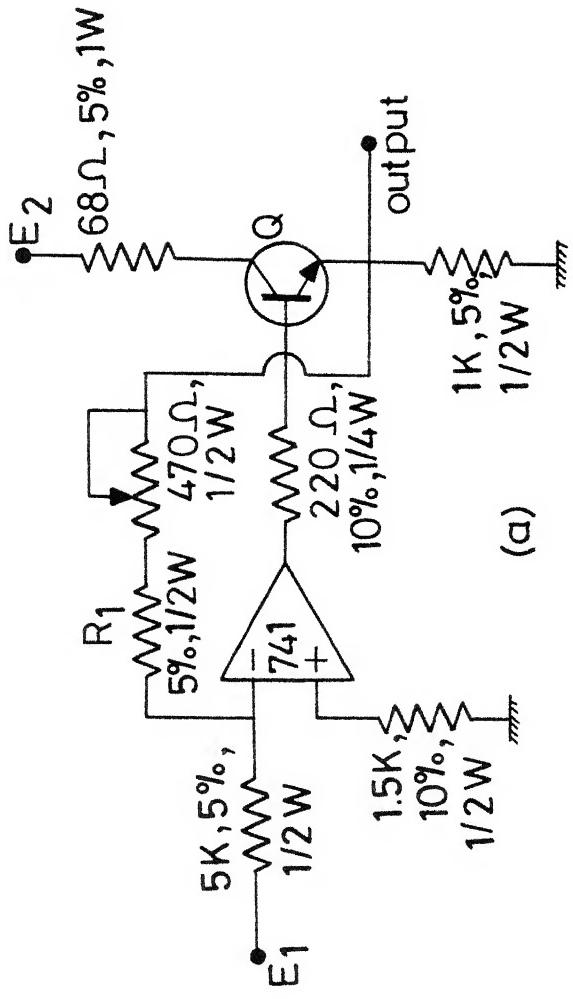
(b) For supply of ±2V to E_i, E_C, E_A, & E_H.

Fig. VI.10   Power supplies derived from ±15V networks I_C power supply.
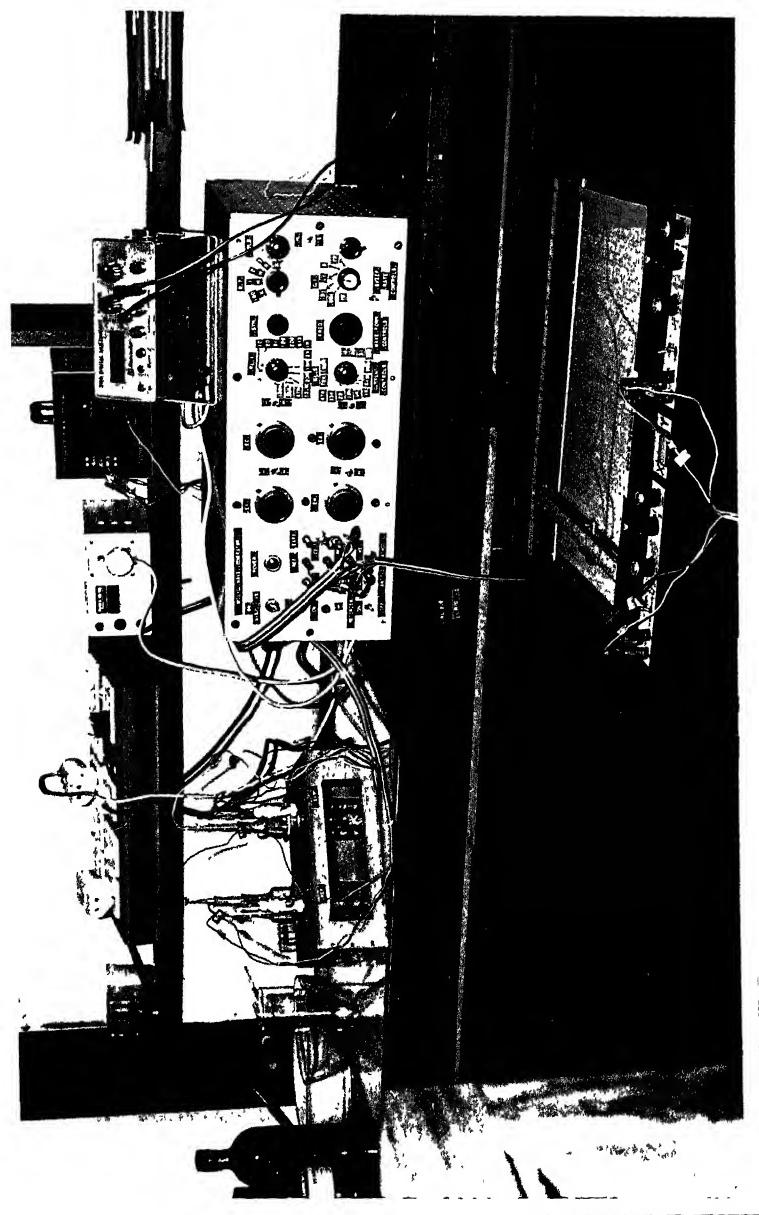
Fig. VI.11.   Photograph of the Cyclic Voltammetric
Instrument with Cell Assembly & Recorder

argon. Reagent grade DMF (E. Merck, Germany) was used directly without any further purification.

VI.3 RESULTS AND DISCUSSION

CV of Trithiazyltrichloride in CH_3CN

The CV-grams were recorded at a platinum working electrode in anhydrous CH_3CN using TEAP as the supporting electrolyte at different scan rates. The concentration of electroactive species $(NSCl)_3$ was kept at 6×10^{-3} M. The potentials reported in this work were referenced to the saturated calomel electrode (SCE). Further, the peak potentials appearing in the discussion and in the figures are at the scan rate of $0.068 \ V.s^{-1}$.

The data from CV-grams for the $(NSCl)_3$ in the range 0.00 V to -1.00 V are summarized in Table VI.1. It is well known that $(NSCl)_3$ exists as a monomeric thionitrosyl chloride, [NSCl] in acetonitrile.[27] CV-grams of [NSCl] in the cathodic sweep displayed two distinct reduction peaks at -0.55 V and -0.65 V (Fig. VI.14(a)). The first reduction peak showed the quasireversible behaviour during the anodic scan while the nature of the second peak (-0.65 V) was totally irreversible. The first reduction wave may be due to the formation of radical anion $[NSCl]^{-}$ which on reversal of the scan oxidized to [NSCl].

$$[NSCl] \rightleftharpoons [NSCl]^{\pm} \qquad \qquad ... (5)$$

Table VI.1: Cathodic and anodic peak potentials in a $\sim 6 \times 10^{-3}$ M $(NSCl)_3$, 0.1 M TEAP CH$_3$CN and DMF solutions at different scan rates

Scan rate (mV / sec)	Solvent	E_{pc} in Volts vs SCE	E_{pa} in Volts vs SCE	$\Delta E_p = E_{pa} - E_{pc}$	$E_{1/2} = \dfrac{E_{pa} + E_{pc}}{2}$ Volts
22	CH$_3$CN	-0.545	-0.400	0.155	-0.467
68	CH$_3$CN	-0.550	-0.425	0.125	-0.487
160	CH$_3$CN	-0.550	-0.420	0.130	-0.485
22	DMF	-0.540	-0.400	0.140	-0.470
66	DMF	-0.550	-0.440	0.110	-0.495
160	DMF	-0.560	-0.450	0.110	-0.500

The colour of the [NSCl] solution in CH_3CN was green which became slightly yellowish on reduction. Cathodic and anodic peak currents for this redox process were almost the same except that anodic peak current was slightly less. This phenomenon may be because of instability of $[NSCl]^{\pm}$ radical anion which underwent secondary reactions during the course of experiment. Appearance of second irreversible reduction peak may be possibly because of the formation of dianion. The quasireversible character of the first reduction wave was shown by the degree of dependence of the ΔE_p value on the potential scan rate (about 60 mV for a ten-fold increase in the scan rate) (Table VI.1). To have a good visibility of the first reduction wave cyclic voltammogram was scaned from -0.30 V to -0.80 V as shown in Fig. VI.14(b).

CV of Trithiazyltrichloride in DMF

Trithiazyltrichloride exists as a monomer [NSCl] in dimethylformamide.[27] CV-gram of [NSCl] in the range 0.00 V to -0.90 V displayed only one well defined reduction peak at -0.550 V (Fig. VI.13(a)(b)) during the cathodic scan which may again be due to the formation of radical anion $[NSCl]^{\pm}$ and it underwent quasireversible oxidation during the anodic scan. The peak currents, I_{pa} and I_{pc}, were almost similar which indicated that the radical anion is more stable in DMF[28] as compared to that in CH_3CN.

Effect of Added $[RhCl(PPh_3)_3]$ on the CV-gram of $(NSCl)_3$ in CH_3CN

In the $\sim 6 \times 10^{-3}$ M $(NSCl)_3$ solution in $CH_3CN \sim 3 \times 10^{-3}$ M $RhCl(PPh_3)_3$ was added and was allowed to stand for a minute. The CV-gram of the above solution showed reduction peak at -0.55 V during the cathodic scan.(Fig.VI.15(a)) which was exactly at the same position as observed in the CV gram of pure $(NSCl)_3$ in CH_3CN. On the scan reversal oxidation ocurred at -0.350 V which indicated a small anodic shift. The shape of the CV-gram was quite different from that observed for pure $(NSCl)_3$ (Fig. VI.14(b)). Cathodic peak is very prominent while the anodic oxidation peak is suppressed, indicating the rapid consumption of the radical anion $[NSCl]^{\pm}$ formed during the cathodic sweep in some chemical reaction. It may possibly be due to the presence of rhodium(I) complex $RhCl(PPh_3)_3$ which gave one electron easily to NS free radical (formed from the disproportionation of $[NSCl]^{\pm}$) to form NS^- species. Rhodium(II) thus formed transfered again one more electron to another molecule of NS radical to form NS^-. Thionitrosyl anion (NS^-) thus formed attacked rhodium(III) and formed the rhodium(III) thionitrosyl complex (Scheme VI.I):

SCHEME VI.I

$$[NSCl] \rightleftharpoons [NSCl]^{\pm} \longrightarrow NS^{\cdot} + Cl^-$$

$$\downarrow [RhCl(PPh_3)_3]$$

$$Rh^{3+}-NS^- + NS^- + Cl^- \xleftarrow{[NSCl]^{\pm}} NS^- + Rh^{2+}$$
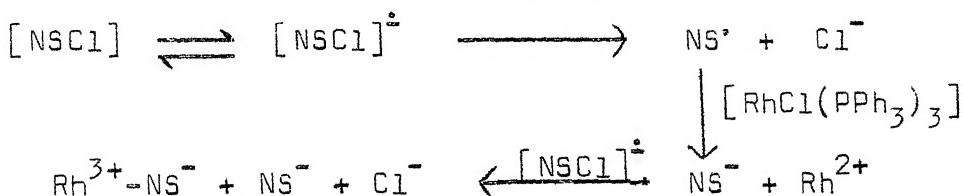
Above mechanism was further corroborated by the fact that we have isolated $[Rh(NS)Cl_2(PPh_3)]_2$ from the above mixture which has already been prepared in our laboratory[26] by reacting $[RhCl(PPh_3)_3]$ with $(NSCl)_3$ in THF.

Effects of Added $NiCl_2(PPh_3)_2$ and $Ru(CO)_3(PPh_3)_2$ on the CV-gram of Trithiazyltrichloride in CH_3CN

In approx. 6×10^{-3} M $(NSCl)_3$ solution (ca. 3×10^{-3} M) $[NiCl_2(PPh_3)_2]$ was added and was allowed to react for a minute. CV-gram of the above mixture showed exactly similar pattern as that obtained for $[RhCl(PPh_3)_3]$ Fig. VI.15(b) (i.e., anodic current was negligible as compared to cathodic current). Since S_4N_4 was recovered from the solution after the CV-gram was taken, it is possible that the radical anion, $[NSCl]^{\overset{\bullet}{-}}$ first disproportionated into NS· radical which catalytically got polymerized to give S_4N_4 (Scheme VI.II). Exact catalytic nature of $[NiCl_2(PPh_3)_2]$, however, was not established. Similar results

SCHEME VI.II

$$4[NSCl]^{\overset{\bullet}{-}} \longrightarrow 4\ NS^{\bullet} + 4\ Cl^{-}$$

$$\downarrow \text{tetramerise}/Ni^{2+}$$
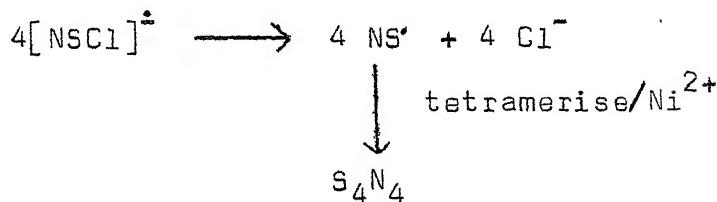
$$S_4N_4$$

were obtained when $[Ru(CO)_3(PPh_3)_2]$ was added in place of $[NiCl_2(PPh_3)_2]$. From the CV cell solution after the experiment was over $[Ru(CO)_2Cl_2(PPh_3)_2]$ and $[S_4N_4]$ were isolated. The

same products were also isolated when reaction of $(NSCl)_3$ with
$[Ru(CO)_3(PPh_3)_2]$ was carried out in THF separately.[29] This
corroborated the removal of Cl^- ions from $[NSCl]^{\dot{-}}$ with the
formation of thionitrosyl radical $(NS^\cdot)$ which tetramerized to
form $[S_4N_4]$ (Scheme VI.III):

<div align="center">

SCHEME VI.III

</div>

$$4[NSCl]^{\dot{-}} \longrightarrow 4 \ NS\cdot + 4 \ Cl^-$$

$$\downarrow [Ru(CO)_3(PPh_3)_2]$$

$$S_4N_4 + 2[Ru(CO)_2Cl_2(PPh_3)_2]$$
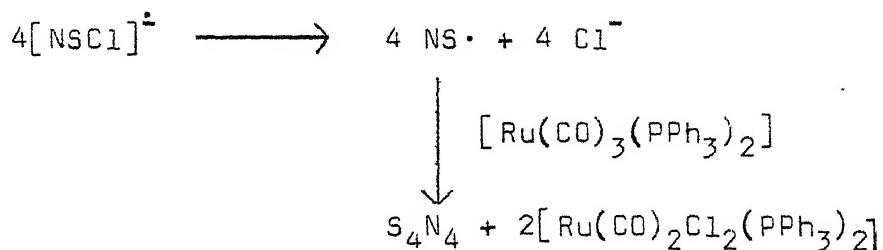
Effect of added $RuCl_2(PPh_3)_3$ and $RuCl_3(AsPh_3)_2 \cdot CH_3OH$ on the CV-gram of Trithiazyltrichloride

In approx. 6×10^{-3} M $(NSCl)_3$ solution in CH_3CN approx.
1×10^{-3} M $[RuCl_2(PPh_3)_3]$ was added and the solution was kept for
a minute. In the cathodic sweep, a steep rising current hyste-
resis curve was observed (Fig. VI.15(c)). The anodic curve
recorded after reversal of the potential scan passed through
the cathodic curve. This peculiar kind of pattern is generally
observed when some reduced solid product gets deposited on the
electrode as reported for systems Co(II)-SCN$^-$,[30] Co(II)-S$_2$O$_3^{2-}$ [31]
and Fe(II)-S$_2$O$_3^{2-}$.[32] The difference observed between the
potential of the steeprise of the current on the cathodic
curve and the potential of the fall of the current on the anodic

curve may be regarded as a crystallization over potential. One well defined oxidation peak was also observed at -0.575 V which is possibly because of the formation of radical cation $[NSCl]^{\overset{+}{\cdot}}$ as shown in the Scheme VI.IV. Thionitrosyl cation (NS^+) thus

SCHEME VI.IV

$$[NSCl] \rightleftharpoons [NSCl]^{\overset{+}{\cdot}}$$

$$[Ru(II)-NS^+] \overset{\longleftarrow}{\underset{[RuCl_2(PPh_3)_3]}{}} NS^+ + Cl^{\bullet}$$
$$\overset{+}{Cl_2}$$
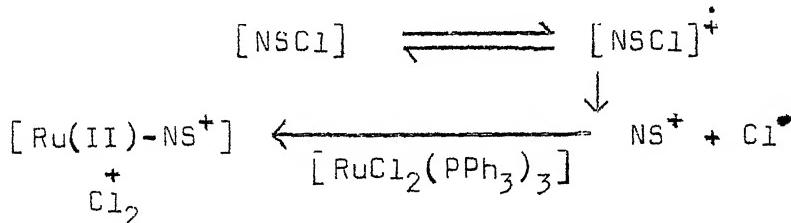
formed may be coordinated with Ru(II) with the evolution of chlorine gas. Infact the crude obtained from the electrochemical cell showed a sharp infrared absorption band at 1300 cm^{-1} which is a characteristic band of coordinated NS^+ [33] and chlorine gas smell was also observed.

Added $RuCl_3(AsPh_3)_2 \cdot CH_3OH$ showed exactly the same pattern as shown by $[RhCl(PPh_3)_3]$ except that an additional sharp cathodic peak at -0.51 V was observed (Fig. VI.15(d)(e)). Similar kind of behaviour was observed in the CV-gram of Na_2SO_3 in which the origin of the sharp peak was explained due to irreversible reduction of sulfur (formed due to some chemical reaction) into sufide.[34] In our system there were ample opportunities of the formation of SO_3^{2-} because of the presence of traces of moisture as shown in equations (7) and (8).

$$NSCl + H_2O \rightleftharpoons HNSO + HCl \qquad \ldots (7)$$
$$HNSO + 2H_2O \rightleftharpoons (NH_4)_2SO_3 \qquad \ldots (8)$$
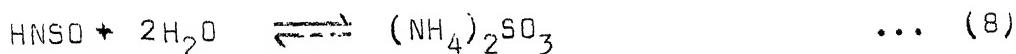
Possibly solvated methanol accelerated the above process.

LEGEND TO THE FIGURES

Fig. VI.12.   Cyclic Voltammograms of the compounds in aqueous

medium; Concentration $\sim$ 1 x 10^{-3} M; Supporting

electrolyte, 0.1 M NaCl; Sweep rate 0.068 V/sec.

(a) $K_4Fe(CN)_6$

(b) $[Ru(NH_3)_5Cl]Cl_2$

Fig. VI.13.   Cyclic Voltammograms of $(NSCl)_3$ in DMF; Concen-

tration $\sim$ 6.0 x 10^{-3} M; Supporting electrolyte,

0.1 M TEAP; Sweep rate 0.068 V/sec.

(a) Sweep range 0 to 0.9 V

(b) Sweep range 0 to 0.7 V

Fig. VI.14.   Cyclic Voltammograms of $(NSCl)_3$ in CH_3CN;

Concentration $\sim$ 6.0 x 10^{-3} M; Supporting electro-

lyte, 0.1 M TEAP; Sweep rate 0.068 V/sec.

(a) Sweep range 0.0 to 1.00 V

(b) Sweep range 0.3 to 0.8 V

Fig. VI.15.   Effect of added complexes (ca. 1.0 x 10^{-3} M) on

the CV-gram of $(NSCl)_3$, (ca. 6.0 x 10^{-3} M) in

CH_3CN, Supporting electrolyte, 0.1 M TEAP; Sweep

rate, 0.068 V/sec.

(a) Effect of added $[RhCl(PPh_3)_3]$
(b) Effect of added $[NiCl_2(PPh_3)_2]$
(c) Effect of added $[RuCl_2(PPh_3)_3]$
(d) Effect of added $[RuCl_3(AsPh_3)_2].CH_3OH$, first
scan
(e) Effect of added $[RuCl_3(AsPh_3)_2].CH_3OH$, second
scan.

(a)

25μA

MICROAMPERE

0.4   0.2   0.0

−E(volts) Vs. SCE

CYCLIC VOLTAMMOGRAM

Fig. VI.12

(b)

10μA

MICROAMPERE

0.0   0.2   0.4

−E (volts) Vs. SCE

CYCLIC VOLTAMMOGRAM

Fig.VI.12

CYCLIC VOLTAMMOGRAM

Fig. VI.13

(a)

200 μA

MICROAMPERE

0.0   0.2   0.4   0.6   0.8   1.0

-E (volts) Vs. SCE

CYCLIC VOLTAMMOGRAM

Fig. VI.14

(b)

50μA

MICROAMPERE

0.3   0.5   0.7

−E (volts) Vs SCE

CYCLIC VOLTAMMOGRAM

Fig. VI.14

(a)

50μA

MICROAMPERE

−E (volts) Vs. SCE

CYCLIC VOLTAMMOGRAM

Fig. VI.15

CYCLIC VOLTAMMOGRAM

Fig.VI.15

(c)

50 μA

MICROAMPERE

−E (volts) Vs. SCE

CYCLIC VOLTAMMOGRAM

Fig. VI.15

CYCLIC VOLTAMMOGRAMS
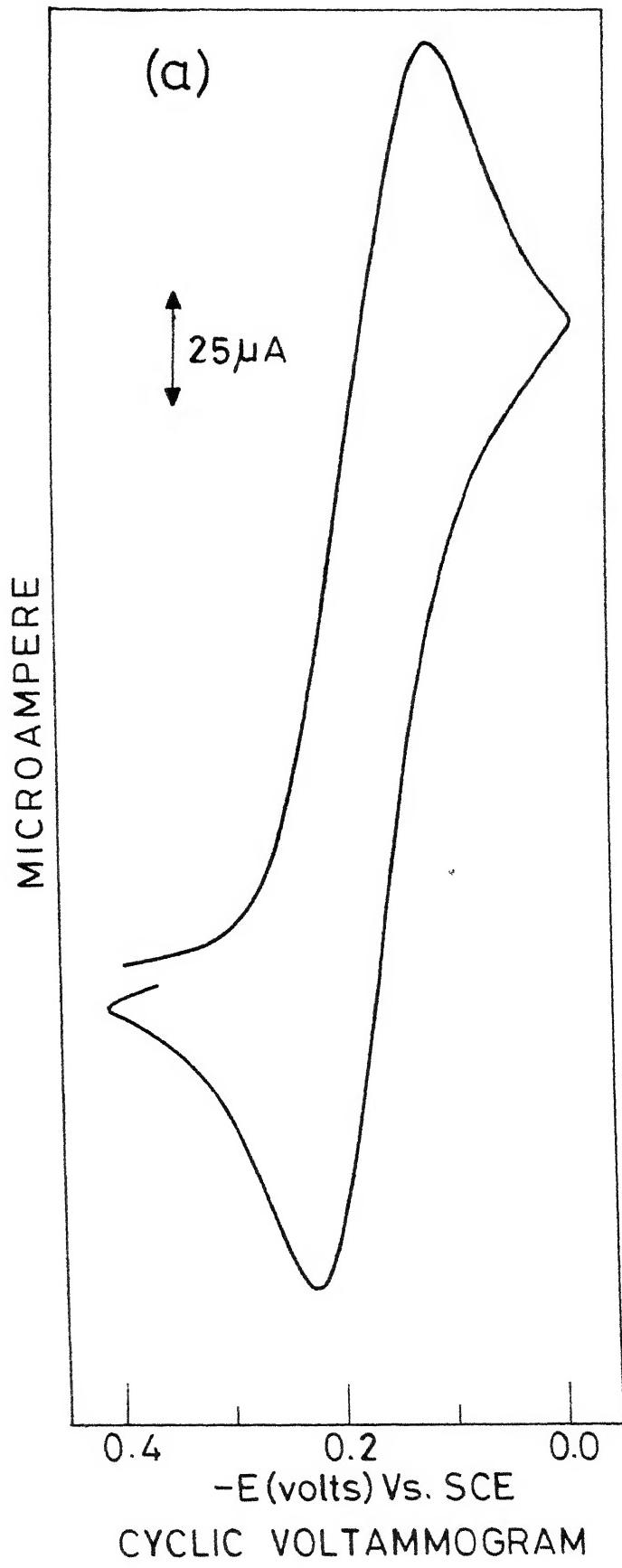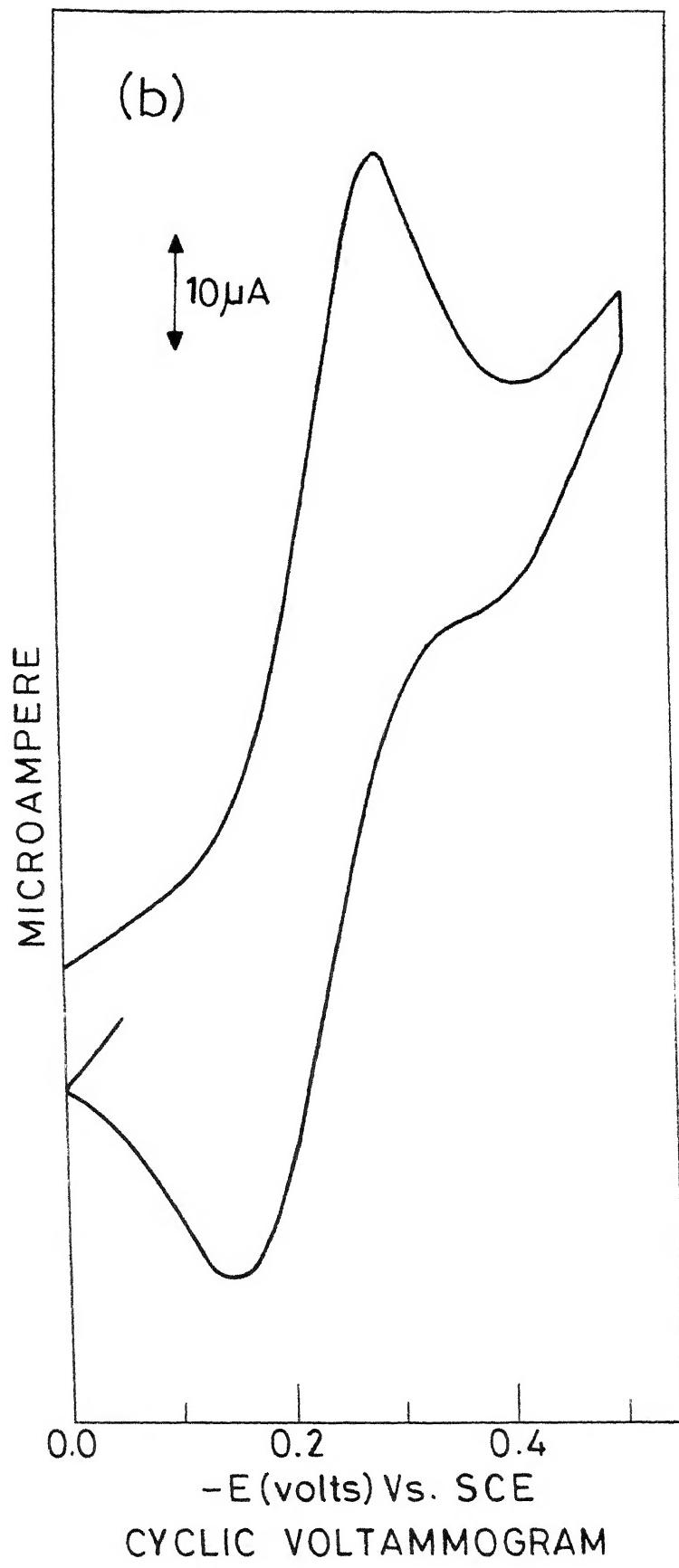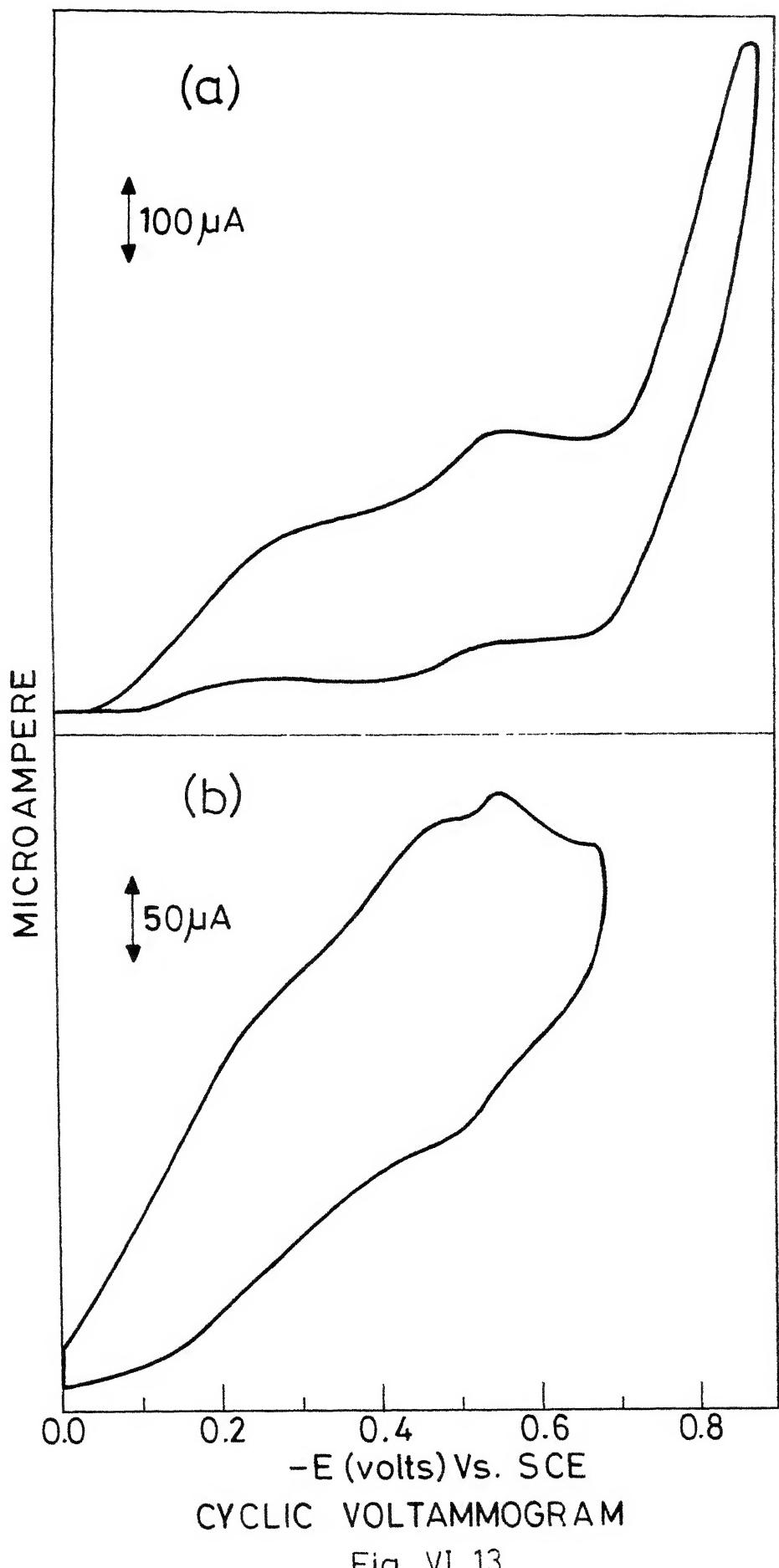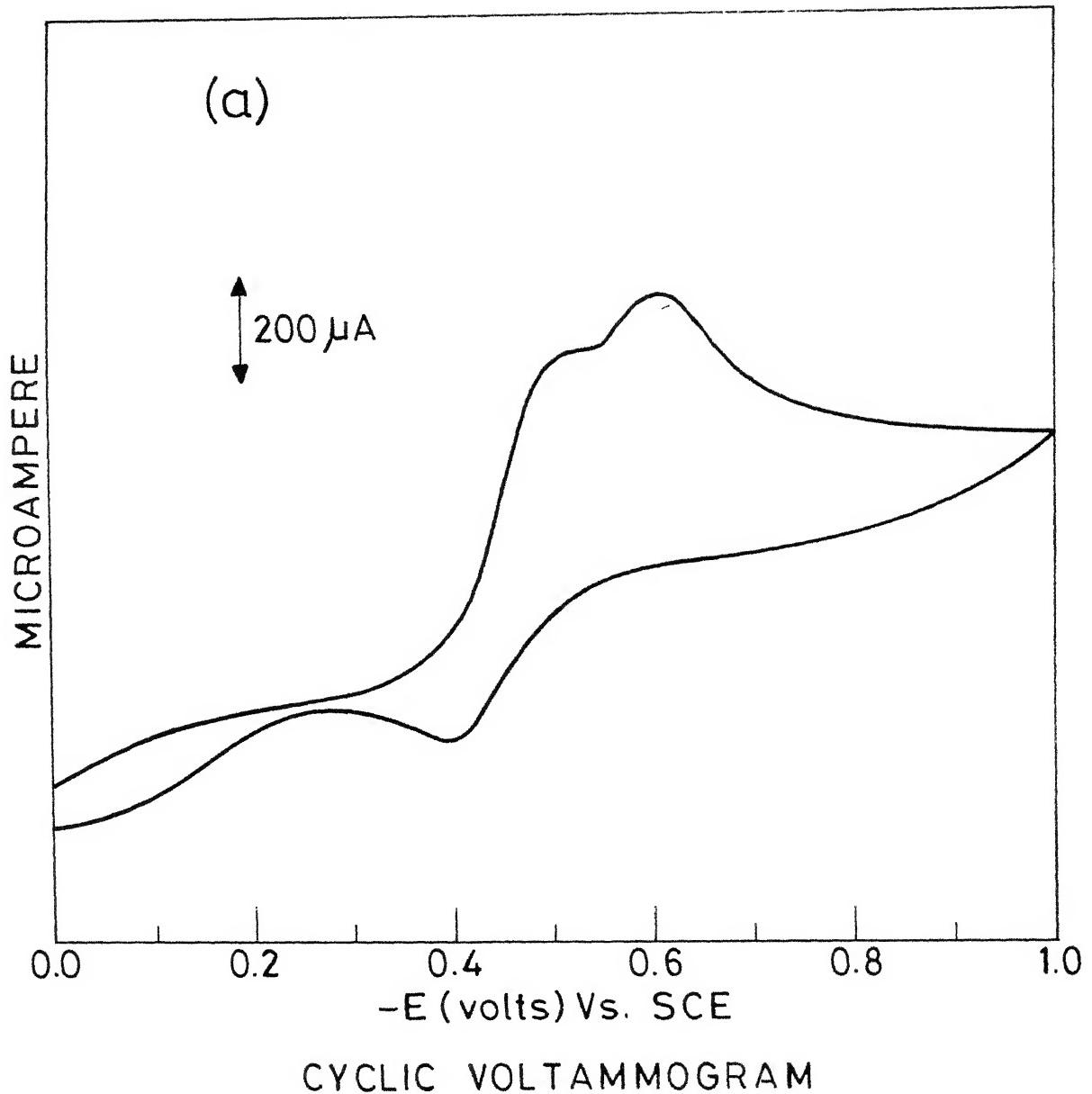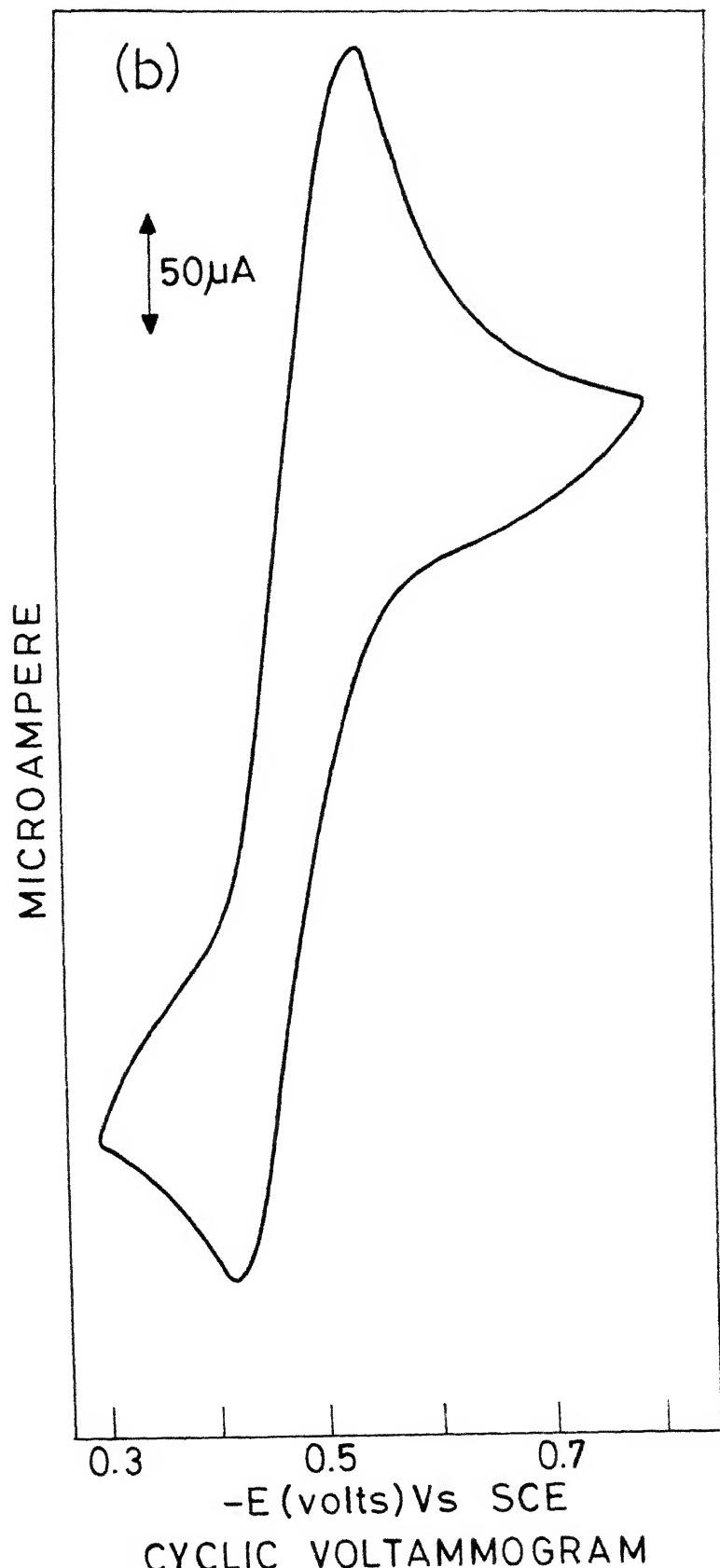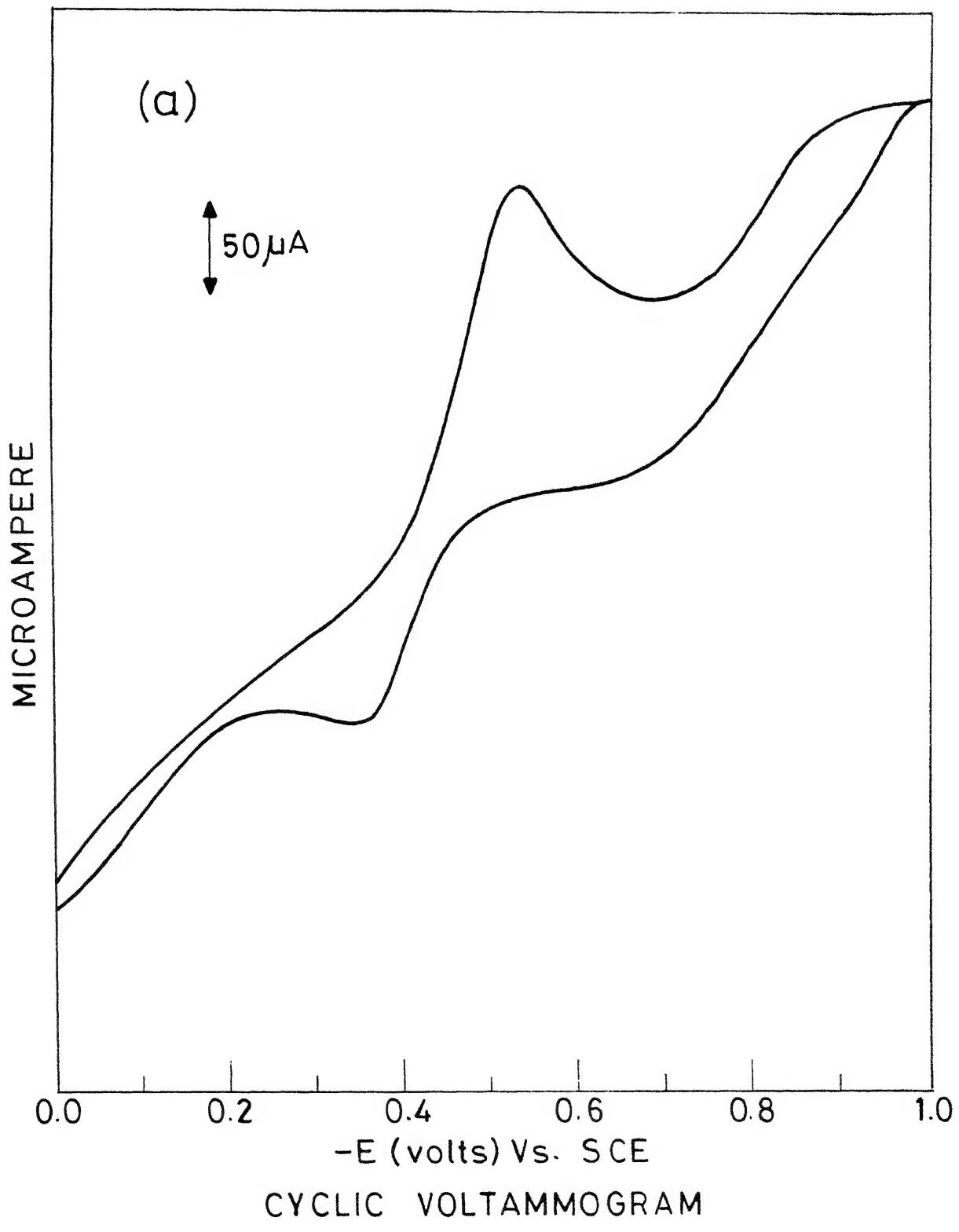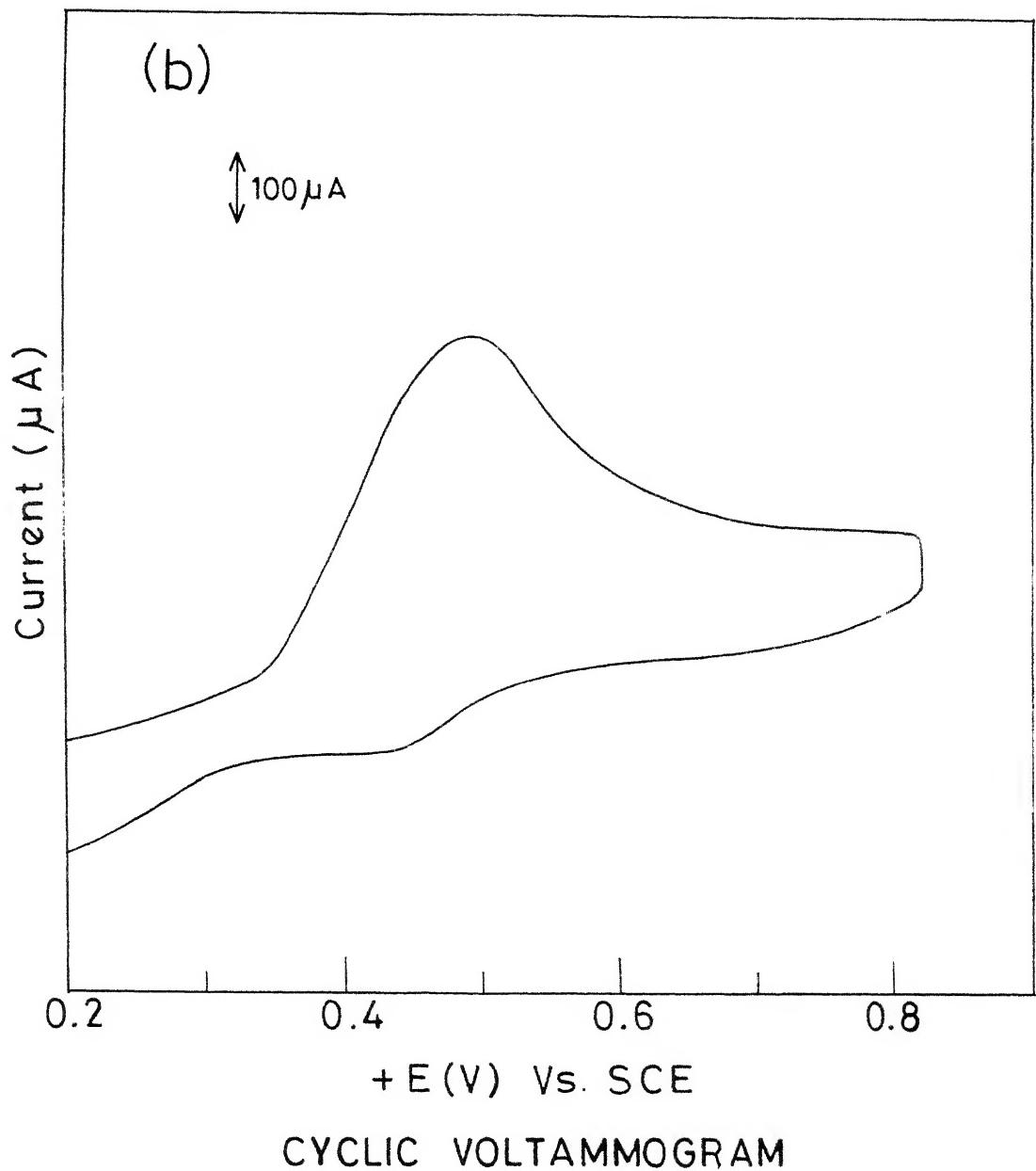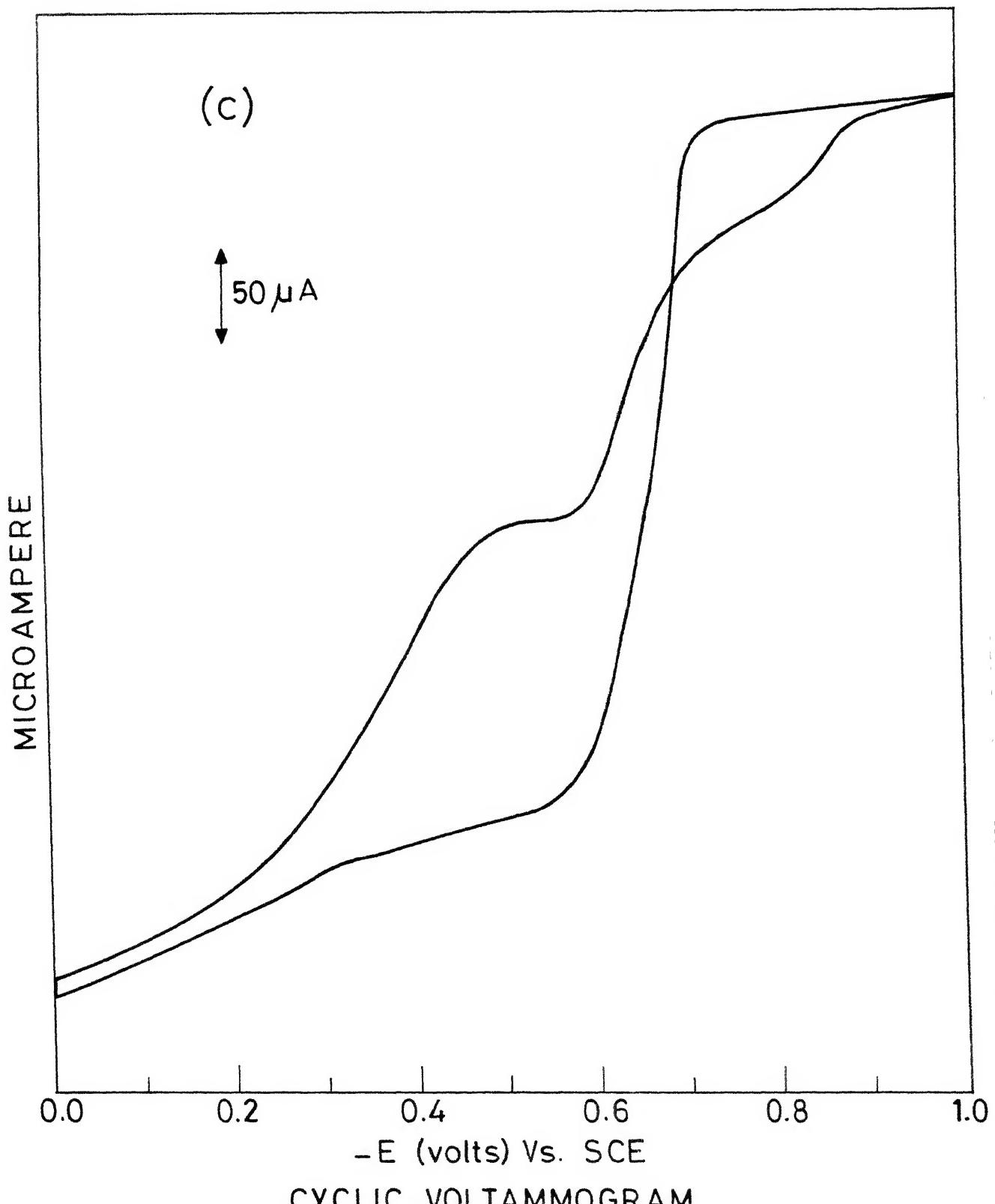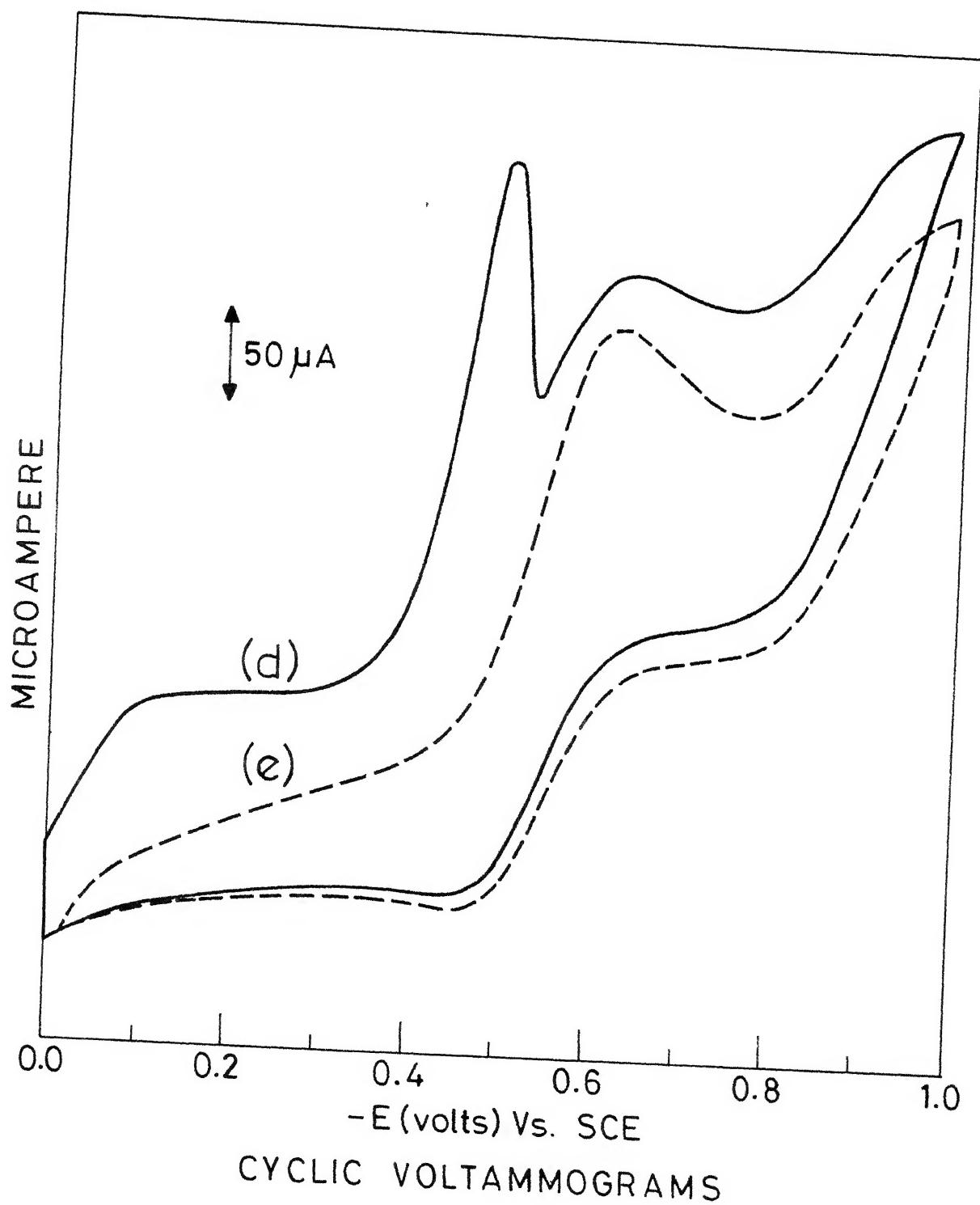
Fig. VI.15

REFERENCES

1. J.B. Headridge and D. Pletcher, J. Polarogr. Soc., 13, 107 (1967).

2. G. Bianchi, T. Mussini and C. Traini, Chim. Ind. (Milan), 45, 1333 (1963).

3. P.G. McCormic and H.S. Swofford Jr., Anal. Chem., 41, 146 (1969).

4. C. Tamayo Garcia, A.G. Calandra and A.J. Arvia, Electrochim. Acta, 17, 2181 (1972).

5. A.G. Calandra, C. Tamayo, J. Herrera and A.J. Arvia, Electrochim. Acta, 17, 2035 (1972).

6. B. Gino, M.G. Antonio and M. Franco, Electroanal. Chim. and Interfacial Electrochem., 55, 91 (1974).

7. J.W. Tweh and A.G. Turner, Inorg. Chim. Acta, 48, 173 (1981).

8. L. Meites, Polarographic Techniques, 2nd Edn., New York, Wiley, 413 (1965).

9. J.E.B. Randles, Trans. Faraday Soc., 44, 327 (1948); A. Sevcik, Coll. Czech. Chem. Commun., 13, 349 (1948).

10. R.S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964).

11. R.S. Nicholson, Anal. Chem., 37, 1351 (1951); P. Delahey, J. Am. Chem. Soc., 75, 1190 (1953).

12. R.N. Adams, Electrochemistry at Solid Electrodes, Marcel-Dekker, Inc., N.Y., 270 (1969).

13. M.M. Nicholson, J. Am. Chem. Soc., 76, 2539 (1954).

14. D.T. Sawyer and J.L. Roberts Jr., Experimental Electrochemistry for Chemists, John Wiley and Sons, N.Y., 45, (1974).

15. J.B. Headridge, Electrochemical Techniques for Inorganic Chemists, Academic Press, N.Y., 7 (1969); Reference No. 14, page 34.

16. M.S. Spitzer, Ph.D. Thesis, University of Michigan, p. 163 (1965).

17. W.L. Underkoffler and I. Shain, Anal. Chem., 35, 2778 (1963).

18. J.G. Mohanty and A. Chakravorty, Indian J. Tech., 15, 209 (1977).

19. A. Weissberger and B.W. Rositer, Technique of Chemistry, Wiley Interscience, N.Y., Vol. 1, Part IIA, p. 515 (1971).

20. Reference No. 12, p. 37.

21. E.R. Brown, T.G. McCord, D.E. Smith and D.D. Deford, Anal. Chem., 38, 1119 (1966).

22. R.L. Myers and I. Shain, Chem. Instr., 2, 203 (1969).

23. Reference No. 12, p. 148.

24. W.L. Jolly and K.D. Maguire, Inorg. Synth., 9, 102 (1967); J.A. Osborn and G. Wilkinson, Inorganic Synth., 10, 68 (1968); P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., 12, 237 (1970); N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorg. Synth., 15, 50 (1974); K. Natarajan, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India (1976).

25. References 14, p. 203.

26. Ph.D. Thesis, K.K. Pandey, Indian Institute of Technology, Kanpur, India (1980).

27. T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, Inorg. Chem., 18, 3548 (1979).

28. J.R. Jezorek and H.B. Mark Jr., J. Phys. Chem., 74, 1627 (1970).

29. K.C. Jain and U.C. Agarwala, unpublished work.

30. E. Itabashi, J. Electroanal. Chem., 88, 205 (1978);
    E. Itabashi, J. Electroanal. Chem., 97, 33 (1979).

31. E. Itabashi, J. Electroanal. Chem., 91, 339 (1978).

32. E. Itabashi, J. Electroanal. Chem., 103, 189 (1979);
    Z. Stojeck and Z. Kublic, J. Electroanal. Chem., 70,
    317 (1976).

33. K.K. Pandey and U.C. Agarwala, Z. Anorg. Allgm. Chem.,
    461, 231 (1980).

34. D.T. Sawyer, Electroanal. Chem., 15, 181 (1967).

SUMMARY

and

SCOPE FOR FUTURE WORK

Nitrosyl forms stable complexes with most of the metal ions which have been known for over thirty years. It is, however, only in the last decade that the nature of bonding and reactivities of nitrosyls have been given serious consideration. In most of these studies NO gas has generally been utilized to introduce nitrosyl functionality in transition metal complexes. However, the reactions of NOX (X = Cl, Br, Br_3, NO_2) with coordinatively unsaturated molecules may be additive or with coordinatively saturated molecules, substitutive, each NOX added may displace ligands capable of donating to the total of four electrons to the metal. The possibility of an oxidative addition reaction will not only result in nitrosylation reaction, but it might be able to oxidize metal ions to a higher oxidation state. Under these situations the reactions might make a very convenient

synthetic route to metal nitrosyls. Even if the metal is not oxidized, the nitrosylation reaction is at least expected. In view of this the reactions of N_2O_3, $NOBr_3$, NOBr and NOCl have been taken up with a few heavy transition metal ions and their complexes.

In addition, the studies on analogous thionitrosyl complexes is in the embryonic state, which may be owing to the lack of thionitrosylating agent. A few thionitrosyl complexes have been prepared: (1) by reacting elemental sulfur, propylene sulphide or disulfur dichloride with coordinated nitrido ligand in the complexes, and (2) by the reactions of trithiazyltrichloride with $Na[\eta^5-C_5H_5)Cr(CO)_3]$, a few rhodium complexes and with $RhCl_3 \cdot xH_2O$, $OsCl_3 \cdot xH_2O$ or $RuCl_3 \cdot xH_2O$ in presence of triphenylphosphine and triphenylarsine in tetrahydrofuran. Although ruthenium forms more nitrosyls than any other element, only two thionitrosyl complexes of ruthenium are reported. Besides one thiazate complex of iridium $[Ir(CO)-(NSO)Cl_2(PPh_3)_2]$ has so far been reported in the literature. The syntheses of thionitrosyl complexes of ruthenium, iridium and rhodium and the thiazate complexes of rhodium have, therefore, been taken up.

The first chapter of the thesis describes in brief the scope of the work, the chemistry of the thionitrosyl group, NS , thionitrosyl complexes, bonding modes of nitric oxide in transition metal complexes with special emphasis to {RuNO} system, a

brief but up-to-date literature survey of {RuNO}[6], {RuNO}[7], {RuNO}[8], {RuNO}[10], nitro, nitrato complexes of ruthenium, platinum and palladium, thiazate complexes and cyclic voltammetric studies on sulfur-nitrogen complexes.

In Chapter II, the syntheses and reactions of novel ruthenium complexes having both NS and NO groups have been discussed. The compounds synthesized and studied are $[Ru(NS)_2Cl_2(PPh_3)_2]\cdot S$ (S = CH_2Cl_2, $CHCl_3$ or $CHBr_3$), $[Ru(NO)-(NS)ClX(PPh_3)_2]$ (X = Cl or Br), $[Ru(NSOH)(NS)Cl(PPh_3)_2]\cdot\frac{1}{2}CH_2Cl_2$, $[Ru(CO)(NS)Cl(PPh_3)_2]_2\cdot CH_2Cl_2$, $[RuCl_2Br(NS)(AsPh_3)_2]$ and $[Ru(NO)X_3(PPh_3)_2]$ (X = Cl or Br). Dithionitrosyl complex $[Ru(NS)_2Cl_2(PPh_3)_2]\cdot S$ contains terminal, linear (NS^+) and bent (NS^-) mode of bonding. Presence of NS^+ and NS^- in $[Ru(NS)_2Cl_2-(PPh_3)_2]\cdot S$ has been confirmed by the reactions of electrophiles NOX (X = Cl, Br, Br_3 or NO_2) and nucleophile (OH^-). Reactions of $[Ru(NS)_2Cl_2(PPh_3)_2]\cdot S$ with NOX resulted in the formation of $[Ru(NO)(NS)ClX(PPh_3)_2]$.

Third chapter deals with the syntheses of thiazate complexes of rhodium $[Ru(CO)(H_2O)(NSO)Cl(PPh_3)]$, $[Ru(H_2O)(NSO)_2-Cl(PPh_3)]_2$, $[Rh(H_2O)(NSO)_2Cl(PPh_3)_2]$, thionitrosyl complex of iridium, $[Ir(NS)Cl_2(PPh_3)_2]$ and new route for the synthesis of NS-bridge complex $[Ru(NS)Cl_2(PPh_3)]_2$.

Chapter four deals with the products resulted in the reactions of $RuCl_3\cdot xH_2O$ with NOX (X = Cl, Br, Br_3 or NO_2) in presence of triphenylphosphine, triphenylarsine and

triphenylstibine. Reactions of NOX with some ruthenium complexes, $[RuHCl(CO)(PPh_3)_3]$, $[Ru(CO)_3(PPh_3)_2$ and $RuCl_3(AsPh_3)_2 \cdot CH_3OH$ have also been described. Compounds of the type $[Ru(NO)ClX_2L_2]$ (X = Cl or Br; L = PPh_3, $AsPh_3$ or $SbPh_3$) and $[Ru(CO)_2X_2(PPh_3)_2]$ (X = Cl or Br) have been obtained and studied. One nitro-nitrato complex $[Ru(NO_2)(NO_3)(CO)_2-(PPh_3)_2]$ has also been synthesized.

Chapter five describes the interesting oxidative addition reactions of dinitrogen trioxide with tetrakis triphenylphosphine-palladium(0) and tetrakis triphenylphosphine-platinum(0) in presence and absence of oxygen. Reactions of NOX (X = Cl, Br, Br_3) with $Pd(PPh_3)_4$, $PdCl_2$ and H_2PtCl_6 in presence of PPh_3 and $AsPh_3$ have also been described. These reactions resulted in the formation of complexes $[M(NO_2)_2-(PPh_3)_2]$, $[M(NO_2)(NO_3)(PPh_3)_2]$, $[MCl_2(PPh_3)_2]$, $[MCl_2(AsPh_3)_2]$ (M = Pd or Pt), $[PdBr_2(AsPh_3)_2]$, $[PdBr_2(PPh_3)_2]$ and $[Pd_2Br_4(PPh_3)_2]$.

Electrochemical behaviour of NO, N_2O_4, NO_2, N_2O_3, etc. have been known for the last twenty years but no report pertaining to the studies on their thioanalogues except S_4N_4 is available. Due to the non-availability of a commercial indigenous cyclic voltammetric instrument, a simple cyclic voltammetric set-up has been fabricated by using indigenous materials which forms the first part of Chapter VI. The second part deals with the cyclic voltammetric behaviour of trithiazyl-

trichloride in acetonitrile and dimethylformamide. Quasi-reversible behaviour of the redox process $[NSCl] \rightleftharpoons [NSCl]^{\dot{-}}$ was observed and the effects of added transition metal complexes have been investigated.

A few of so many fascinating problems related to the chemistries of nitrosyl, thionitrosyl and thiazate complexes are as follows:

(1)   Reactions involving electrophilic and nucleophilic attack on the coordinated thionitrosyl in the complexes.

(2)   Syntheses and reactions of thionitrosyl complexes of the other transition and non-transition metal ions.

(3)   Syntheses of the complexes having NS group coordinated through its sulfur end.

(4)   Reaction of coordinated NS group with thiophilic agents to synthesize nitride complexes.

(5)   Reactions of nitrosyl complexes with trithiazyltrichloride at low temperature to obtain the NS bridge complexes.

(6)   Syntheses and reactions of thiazate complexes of the other transition metal ions.

(7)   XPS and X-ray crystal structural studies of thionitrosyl complexes.

(8)   Syntheses of some new thionitrosylating and thiazating agents.

(9)   Effect of temperature on the stability of radical
       anion $[NSCl]^{\cdot -}$.

(10)   Effect of surfactants on the formation and reactions
       of nitrosyl and thionitrosyl complexes of various
       transition metal ions.

LIST OF PUBLICATIONS

A. Accepted

(1) Interaction of dinitrogentrioxide with palladium(0) and Pt(0) complexes,
   K.C. Jain, K.K. Pandey, and U.C. Agarwala,
   Z. anorg. allgem. Chem., 21, 12 (1981).

* (2) Thionitrosyl complexes of rhodium,
   K.C. Jain, K.K. Pandey, S.S. Katiyar, and
   U.C. Agarwala,
   XXI Int. Conf. Coord. Chem. France (1980).

(3) Reactions of NOX (X = Cl, Br, Br_3 or NO_2) with $RuCl_3 \cdot xH_2O$, H_2PtCl_6 and $PdCl_2$ in presence of PPh_3, $AsPh_3$ and $SbPh_3$,
   K.C. Jain, K.K. Pandey, R. Parashad, T. Singh, and U.C. Agarwala,
   Ind. J. Chem., 19A, 1089 (1980).

* (4) Thionitrosyl complexes of rhodium,
   K.K. Pandey, K.C. Jain, and U.C. Agarwala,
   Inorg. Chim. Acta, 48, 23 (1981).

(5) Interaction of NOCl, NOBr, $NOBr_3$ and $NONO_2$ with ruthenium complexes,
   K.C. Jain, K.K. Pandey, and U.C. Agarwala,
   Ind. J. Chem. (in press).

* (6) Hyponitrite complexes of rhodium,
   K.K. Pandey, K.C. Jain, and U.C. Agarwala,
   Ind. J. Chem. (in press).

(7) Thiazate complexes of rhodium,
   K.C. Jain, K.K. Pandey and U.C. Agarwala,
   Ind. J. Chem. (in press).

B. Communicated

(8) Synthesis and reactivities of the first dithionitro-
syl and nitrosyl-thionitrosyl complexes of ruthenium,
K.C. Jain, K.K. Pandey, and U.C. Agarwala,
Inorg. Chim. Acta.

(9) Cyclic Voltammetric studies of $(NSCl)_3$ in different
aprotic solvents and the effect of added transition
metal complexes,
K.C. Jain, R. Parashad, K.K. Pandey, and U.C.
Agarwala,
Inorg. Chim. Acta Lett.

C. Under Preparation

(10) Reaction of $(NSCl)_3$ with $Ru(CO)_3(PPh_3)_2$, $RuHCl(CO)-$
$(PPh_3)_3$, $IrHCl_2(PPh_3)_3$, $Rh(NO)Br_2(PPh_3)_2$ and
$RhH(PPh_3)_4$,
K.C. Jain and U.C. Agarwala,
Z. Anorg. Allgem. Chem.

INSTRUMENTS FABRICATED

(1) Cyclic Voltammetric Instrument.

*(2) Cryostat for doing magnetic measurement with
Gouy method:
temperature control range, -190° to $+200^\circ C$ and
temperature measurement accuracy, $\pm 0.03^\circ C$.

---

*, not included in the thesis.

VITAE

Born on September 11, 1955 at Alwar, Rajasthan, Kailash
Chand Jain passed his Secondary in 1971 from Happy School and
Higher Secondary in 1972 from New Higher Secondary School,
Alwar (affiliated to Board of Secondary Education, Rajasthan).
He did his B.Sc. (Hons.) Chemistry (in 1975) and M.Sc. (in
1977) from Raj Rishi College, Alwar (affiliated to University
of Rajasthan). Subsequently he joined the Ph.D. programme in
the Department of Chemistry, Indian Institute of Technology,
Kanpur in July, 1977 and was appointed as Research Assistant
in January 1981. Presently he is continuing as a Research
Assistant in the same department.